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PROCEEDINGS

CONTENTS.

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Discussion on the Structure of the Atom.

Abstract of Opening Address by Sir E RUTHERFORD

When the Secretary of the Royal Society asked me to open a discussion on the structure of the atom, I very gladly acceded, for I felt that it was a subject which would be of interest to many members of the Society, even if their own investigations are not directly connected with this special field of enquiry I should first like to point out that a large part of the work in modern Physics for the last 20 years has been intimately connected with the problem of the structure of the atom, and several very powerful methods of attack have recently been developed to throw light on its structure The discovery of the negative electron as a constituent of all atoms much widened our conceptions, while the detailed study of radioactive substances has brought to light the remarkable series of transformations that occur in them, resulting in the addition of more than a score of new "transition" elements, which have a limited life, and break up with the emission of intense radiations and of a large amount of energy A study of the scattering of swift α- and β-particles in passing through matter has thrown much light on the structure of the atom, for these particles have such great energy of motion that they actually pass through the individual atoms, and are deflected by the intense electric fields they meet within the atom In addition, the recent methods of studying X-ray spectra by their reflection from a crystal promise to give much valuable information on the modes of vibration of the inner constituents of the atom.

The proof that the negative electron was a constituent of all atoms, and could be released from them by a variety of agencies, gave a great impetus to the study of atomic structure It was soon recognised that a heavy atom must be regarded as a complex structure, consisting of negatively and positively charged particles, which were held in equilibrium mainly by electrical forces A type of atom model, suggested by Lord Kelvin, has been developed and worked out with great detail and skill by Sir J J Thomson, and is now generally known as the "Thomson" atom The atom is supposed to consist of a sphere of uniform positive electrification extending over a distance comparable with the ordinary accepted diameter of the atom, and containing within it a sufficient number of electrons to make it electrically neutral This type of model atom has the great advantage that the distribution and velocities of the component electrons which make up the atom can be worked out mathematically in detail, and it has been shown that the electrons tend to distribute themselves either in rings in one plane or in spherical shells like the coat of an onion Sir J J Thomson has shown that such a model atom imitates in a remarkable way several of the general properties of the actual atoms, and affords a suggestive explanation of the reason why some atoms are electropositive and others electronegative, and of the variation of the properties of atoms with atomic weight as exemplified in the Periodic Law

There is one difficulty, however, that is common to all types of model atoms According to the electromagnetic theory, electrons in orbital motion must radiate energy, but this difficulty has to some extent been removed by the proof of Sir J J Thomson that the orbital motion of a large number of electrons in a ring radiates energy at a very slow rate Although the atom may remain stable for long periods, it must ultimately break up, due to this continuous drain of energy by radiation

While the "model atom" of Sir J J Thomson has performed a very useful service in indicating the general properties of the electrical atom, and has proved very amenable to calculation, it does not seem able without modification to explain some experimental facts that have been brought to light in recent years It has now been definitely established that when swift α-particles pass through a thin film of matter, some of the α-particles are deflected through more than a right angle in consequence of the close encounter of an α-particle with a single atom This result shows that the atom must be the seat of intense electric or magnetic forces General calculation shows that the particular distribution assumed for the positive electricity in the Thomson atom does not admit of sufficiently strong fields to deflect an α-particle through a large angle, unless it be supposed that the positive electricity is concentrated in a very small volume In order to explain such results, I was led to consider the properties of a "nucleus" atom, in which the positive charge and most of the mass of the atom are concentrated within an exceedingly small volume at the centre of the atom The nucleus is surrounded by a distribution of electrons to make it electrically neutral, but extending for a distance from the centre comparable with the diameter of the atom It was supposed that the large single deflection of α particles was due to their passage close to the nucleus, where the field is very intense, and where few, if any, electrons are present Simple calculation shows that the external electrons are incapable of producing more than small scattering of the α particle passing through them Regarding the α particle and nucleus as point charges of electricity, the laws of this large-angle scattering were simply deduced on the assumption that the forces between them were electrical and followed the inverse square law These conclusions were examined in great detail in the experiments of Geiger and Marsden They found, for example, that the number of α-particles scattered through different angles agreed with the theory over a very wide range, and in general they verified all the main predictions of the theory Darwin has recently shown that no other law of force, except the inverse square, is consistent with the experimental results The scattering of high-speed particles like α particles, in their passage through the atom, thus provides us with a powerful method of deducing the intensity of the forces in the atom, and thus throwing light on the structure of the central part of the atom From the magnitude of the scattering at different angles, it is possible to deduce the nucleus charge The value of the charge was found to vary approximately as the atomic weight, and to be equal to about $\frac{1}{2}Ae$, where A is the atomic weight and e the unit of charge On this view, the number of external electrons in the atom is about one half of the atomic weight in terms of hydrogen It is significant that a similar result was obtained by Barkla from consideration of the scattering of X-rays by matter These conclusions were based on the theory of scattering of X-rays by electrons worked out by Sir J J Thomson

From these results, we may consequently conclude that the nucleus charge of gold, for example, atomic weight 197, is about 100 units, and that it is surrounded by 100 electrons. (*Note*—The value of the nucleus charge deduced from its X-ray spectra was shown by Moseley later in the discussion to be 79.) From the radioactive evidence, it appears probable that the α particle is the nucleus of helium and contains two positive charges, and consequently hydrogen can only have a nucleus charge of unity. Van den Broek and Bohr have suggested that the nucleus charge may prove to be the atomic number of the elements when arranged in increasing order of atomic weight. On this view, which has much to commend it, hydrogen has one charge, helium two, lithium three, carbon six, and so on. This important point will be referred to later.

From the scattering of the α-particles by gold, it was deduced that the α-particle must approach to within 3×10^{-12} cm. of the nucleus to be deflected through nearly 180°. This suggested that the nucleus of the atom has dimensions exceedingly minute compared with the sphere of action of the atom, and that, consequently, the positive electricity is very concentrated. This view is strongly supported by some recent experiments of Marsden. On the nucleus theory, an α-particle in a close encounter with a hydrogen atom should set the hydrogen atom in very swift motion. Under the best conditions, the hydrogen atom should gain a velocity about 1.6 times that of the colliding α-particle. To test this point, an intense beam of α-particles was passed through hydrogen. Most of the α-particles were stopped at 20 cm.—the range of the α-particles in hydrogen, but a small number of scintillations on a zinc sulphide screen were observed for a distance up to 90 cm. No such effect is observed in air. There appears to be no doubt that some of the hydrogen atoms are set in such swift motion by the α-particles that they have a range in hydrogen about four times greater than the α particle, and are able to produce visible scintillations. A simple calculation shows that the α-particle must approach within 1.3×10^{-13} cm. of the hydrogen nucleus in order for the latter to gain its great velocity. Now this distance is very small, even smaller than the accepted diameter of the electron, viz., 3.4×10^{-11} cm. This calculation gives a maximum limit to the dimensions of the hydrogen nucleus, and it may be much smaller. For these reasons, I have suggested that the mass of the hydrogen atom may be electrical in origin and that the hydrogen nucleus is the positive electron.

We shall now consider the bearing of the radioactive evidence on the structure of the atom. The expulsion of charged helium atoms in so many of the transformations indicates that the nucleus is composed, at any rate in part, of helium atoms. The energy of expulsion of α-particles can be readily explained by its passage through the strong nucleus field even if it escapes with little initial velocity. The general evidence indicates that the primary β-particles arise from a disturbance of the nucleus. The latter must consequently be considered as a very complex structure on a minute scale consisting of positively charged particles and electrons, but it is premature (and would serve no useful purpose) to discuss at the present time the possible structure of the nucleus itself.

On the nucleus theory, the ordinary properties of the atom are dependent entirely on the nucleus charge, since the value of the latter must determine the electronic distribution. The properties of gravitation and radioactivity which are unaffected by chemical or physical agencies must be ascribed to the nucleus.

Recently Fajans and Soddy have put forward a very important generalisation to explain the variation of chemical properties of the series of elements resulting from the transformation of the radioatoms   They suppose that the expulsion of an α-particle changes the position of the resulting element two groups in the periodic table in the direction of diminishing mass, while an expulsion of a β-particle changes it one in the opposite direction   On the nucleus theory, this supposes that the loss of an α particle (carrying two unit positive charges) *lowers* the nucleus charge by two units, while the loss of a β-particle (carrying one negative charge) *raises* the nucleus charge by one unit. On this view, for example, the elements radium B and radium D should have the same nucleus charge as the end-product of the radium series, which is believed to be lead   It is significant that both radium B and radium D are so closely identical in chemical properties with lead that they are inseparable from it

Numerous examples of a similar kind are known amongst the radioelements   We are thus led to the important conclusion that elements of *different* atomic weights may have identical chemical and physical properties   If the nucleus charges are the same, they should also give nearly identical spectra, for it seems unlikely that the mass of the nucleus will exert much influence   No doubt definite evidence on these points will be soon forthcoming *

A number of cases are known in the radioelements where the nucleus charge differs by unity   Recently some very definite evidence on this point has been obtained by Moseley by entirely distinct methods for a number of ordinary elements   As you know, experimental methods have recently been developed by Bragg, Moseley and Darwin for determining the X-ray spectra of elements by reflection from crystals   The frequency of vibration, which is about 1000 times greater than for the shortest light waves, can be directly deduced from the structure of the crystal   When an element is exposed as anticathode in an X-ray tube, it emits its characteristic radiation and its spectrum is examined by the crystal method   Moseley examined in this way the X-ray spectra of twelve consecutive elements from calcium to nickel   The spectra of all these elements are similar in type, consisting essentially of two strong lines   The frequency of these lines was found to increase by definite *steps* in passing from one element to the next   Without discussing the theory of the origin of these spectra, it suffices to say that the frequency was found to be proportional to $(N - a)^2$ where N was a *whole* number and a a constant about unity   N in this case was a whole number which varied by unity from 20 for calcium to 30 for zinc, and corresponded to the atomic number or nucleus charge   These results thus show clearly that the mode of vibration of the interior of the atom is closely connected with the number N which is believed to be a measure of the nucleus charge   I understand that Mr Moseley has still further experimental results to contribute later in the discussion

I have so far not dealt with the important question of the distribution of the external electrons which make up the atom   It is obvious there are great difficulties on the ordinary mechanics in considering possible distributions, for there is no reason why an electron if disturbed should not always fall into the

* Since the discussion Dr Andrade and I have shown that the strong lines of the γ ray spectrum of radium B are identical with the characteristic X ray spectrum of lead   Evidence has also been obtained by several investigators that the atomic weight of lead formed from radioactive matter differs from that of ordinary lead

nucleus. In order to overcome these difficulties, Bohr has supposed that the electron may take up a number of definite positions with regard to the nucleus, corresponding to what he calls "the stationary states" A radiation of definite frequency is supposed to be emitted when an electron falls from one stationary state to another By introducing a conception connected with Planck's quantum, he has attempted to explain the origin of the series spectra of the simple elements, and has shown that the fundamental frequency is in close accord with experiment The atom of hydrogen is supposed to be the simplest possible structure consisting of a nucleus of unit charge and one electron The complexity of the spectrum in this case is supposed to be due not to the complexity of the atom but to the number of possible stationary states which the electron can take up In a similar way, he supposes the atom of helium to consist of a nucleus of two charges and two electrons, and has given reasons for believing that some recently discovered spectra which have been attributed to hydrogen in reality belong to helium This question is, however, still *sub judice* The structure of a number of elements has been indicated along these lines, supposing that the nucleus charge increases by unity in passing from one atom to the next

Bohr has also discussed the structure of the hydrogen molecule, which is supposed to consist of two hydrogen nuclei with a ring of two electrons rotating between them The heat of combination has been calculated and is in fair accord with the latest experimental data He finds that the helium atom as constructed refuses to unite with another helium atom or with a hydrogen atom This is in agreement with the observed behaviour of helium While it is too early to say definitely whether the theories of Bohr are valid, his contributions to the structure of simple atoms and their spectra are of great importance and interest

In this address I have endeavoured to point out briefly the main lines of attack on this question, and the point of view that at present guides the investigations of myself and others in this most difficult and interesting of problems

Mr H. MOSELEY* The chief difficulty at the present moment in discussing the structure of the atom is that the experimental methods by which we can get anywhere near to the centre of the atom are extremely few We may say that Sir Ernest Rutherford's view of the atom arose originally and is based principally upon the one all-important fact of the scattering of the α-particles The α-particle is the only thing which can penetrate sufficiently deeply into the atom to find out about the central part of the atom If we are ever going to find out what is the structure of the atom, it will be from the middle outwards I want to show you that the X ray spectra of the elements give a rather hopeful method of adding to our information The possibility of analysing the X-ray spectra we owe to the work of Prof Bragg and his son The only way in which the work which I have followed out differs from theirs is that, while they used electrical methods, I have registered the spectra photographically It happens, that when a very large number of elements have to be rapidly investigated the photographic method is much quicker than the electrical method.

* Owing to Mr Moseley's absence from England, the proofs of the stenographic report of his remarks have been corrected for him by Sir Ernest Rutherford. An account of these experiments of Mr Moseley has been given in two papers in the 'Philosophical Magazine,' Dec, 1913, and April, 1914

The first slide shows the most convenient kind of X-ray tube to use for this work. It is simply a very large X-ray tube of 8 litres capacity. The different specimens which are going to be bombarded by the stream of cathode rays, in order to excite their characteristic X-radiations, are mounted on a movable anticathode. These specimens may be in the form of elements, alloys, or compounds. In many cases I have used thin layers of the metallic oxides spread over a plate of nickel, for example. The substances are bombarded by the cathode rays, and the stream of general X-radiation mingled with the characteristic monochromatic rays goes through a fine limiting slit. They pass out in a divergent stream and fall on the reflecting crystal. The peculiarity, as Bragg has shown, of the reflection from crystals of these monochromatic rays is that they are only reflected when there is a certain definite connection between the wave-length and the angle at which they strike the crystal. Possibly only one of the different kinds of radiation will hit the crystal at such an angle that it can be reflected. The reflected rays have this remarkable property that, although the incident beam is divergent, a sharply defined line of about the same breadth as the original slit is found on the photographic plate.

I have examined by this method a large number of elements or their compounds. This slide shows one of the earliest photographs obtained for chromium. There is one extremely strong line and another much fainter line of about 10 per cent. greater frequency.

The spectrum shown for chromium is to be ascribed to "K" characteristic radiation of that element. For elements of atomic weight greater than silver, the spectrum of the "L" series of Barkla has been determined. This spectrum consists mainly of three lines, α, β, γ, which are clearly shown in the spectrum of lanthanum, for example.

In this slide are given the collected results for all the elements that so far I have been able to investigate. I thought that it was better at first to make a general rough survey of the spectra of as many elements as possible, rather than to go into very elaborate detail. We shall first consider the spectra of the K series between aluminium and silver. On this diagram the abscissæ represent the square root of the frequency, and the successive elements are arranged on the vertical scale at equal intervals. Suppose that we begin with aluminium. This represents the very strong line of aluminium corresponding to the strong line of chromium shown previously, and this the weaker line of just a few per cent greater frequency. On coming to silicon, we get exactly the same phenomenon repeated. Here is chlorine, of which at present I have only measured the strongest line. Here are potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, zinc. After a gap we come on to yttrium, zirconium, and so on. You see that the square root of the frequencies of these strong lines plotted against the successive elements placed at equal intervals on this vertical scale fall on a straight line, or rather a line that is straight at first and then bends over slightly. At the latter part we are dealing with very high frequencies, so that whatever is giving this radiation must be treated mathematically as an electromagnetic problem and not as the purely electrostatic problem which is usually taken to suit the lower frequencies. The other fainter lines also fall on a very good straight line, as far as they have been traced, though for the high frequencies only the principal line has been investigated. In making this diagram the elements,

from aluminium upwards, have been arranged not exactly in the order of increasing atomic weight, but in the order of Mendeléeff's periodic table; that is the order of the atomic weight except in the few cases where this clashes with the order of the gradually changing chemical properties   Here, for example, we have the order, chlorine, argon, potassium, calcium, instead of the atomic weight order, chlorine, potassium, argon, calcium.   If the atomic weight order were used the spectrum lines would be thrown completely off this straight line; so we see that we are justified in taking them in the above order

Here, again, the chemical order, iron, cobalt, nickel, is chosen instead of atomic weight order, iron, nickel, cobalt.   It will be observed that the elements have all been spaced at equal distances   This means that in order to get some definite simple relation between the frequency and the element we must ascribe to each element an integer.   This integer can hardly be anything else than the atomic number, the charge on the central nucleus, about which Sir Ernest Rutherford has been speaking, and the fact that the atomic number is about half the atomic weight fits in well with this   We ascribe to aluminium the atomic number 13, though in this point we are not supported by definite experimental evidence   The atomic number of hydrogen is known to be 1, that of helium is 2, so that unless, which is extraordinarily unlikely, the chemists have missed an element before aluminium, the latter, the 13th element, has the atomic number 13   The results show that no elements are missing between aluminium and silver, except for one gap left for a homologue of manganese

Let us next consider the elements of the L series   Fortunately it is not very difficult experimentally to overlap from the K series to the L, that is to say, for some elements both the K series and the L series spectra can be measured

I might mention in passing that the characteristic rays of very long wavelength in this part of the diagram are rather troublesome to examine because they have such extremely small power of penetration.   A radiation of this kind is practically stopped by a centimetre of air   Therefore, it is necessary in investigating them to use a special vacuum spectrometer

In these L series spectra the strongest principal line is called α, and, as before, it is the line of smallest frequency   The points for successive elements lie on a definite regular curve which bends a little and is not quite a straight line   The line β, the next in order of intensity, also lies on a smooth curve which is very much bent.   The third line gives practically a straight line.   There is another line which at present I have only found in the region of the rare earths, although very probably it also appears elsewhere.   The results do not pretend to be in the least complete   The line α for platinum was originally called C by Prof. Bragg. These two lines β and γ were called B before he knew that the line was double. There are also some fainter lines of higher frequency not given on this diagram. What I want to insist upon is the fact that each of the elements has got a spectrum extremely like that of its neighbour.   It is obvious that whatever is giving this spectrum is the corresponding system in the different elements and that its properties gradually change as a function of the atomic number. The continuity of these curves shows that the order in which we have arranged the elements must be correct.

I must say a few words about the way in which this order has been arrived at. In any doubtful instance it has been so arranged that the elements all lie on

a straight line. Chemistry always suspected that there was an unknown homologue of manganese between molybdenum and ruthenium Already in the K series spectra it has proved necessary to leave a space for such an element If this element No. 43 exists at all, it ought to be very easily detected, because the frequencies of the two principal lines of its X-ray spectrum can be predicted with certainty It is necessary also to leave a space for another homologue of manganese between tungsten and osmium The only other doubtful question is the number of the rare-earth elements There has been a very large amount of extremely skilled chemical work done in separating these elements, but it is still a matter of some doubt whether some of them are really simple, or whether they are mixtures. It has been shown that what we used to call ytterbium is a mixture of two elements now known as neo-ytterbium and lutecium Vacant spaces are left for these two elements I find that between erbium and tantalum there are only four places to spare The spectrum of erbium was determined from two specimens The first was a specimen which Sir William Crookes had the very great kindness to give me It gave faintly the strongest line of both elements, thulium I and thulium II There is no doubt that the two different kinds of thulium are exeedingly difficult to separate completely from erbium The erbia also contains traces of dysprosium and of holmium Another sample of erbia contained quite 50 per cent of holmium, or rather of the element whose atomic number is 66, which I take to be holmium Welsbach has actually separated thulium into two different substances, and his assertion that there is a third is based on rather more indirect evidence

We will now look a little more closely into the question of the relation between the square root of the frequency and the atomic number From the curves we saw that the square root of the frequency was a linear function of the atomic number N So we have the frequency $\nu = A (N - b)^2$ If we take the strongest line of the K series, we find that this constant A is numerically equal to $A = \frac{3}{4}\nu_0$, where ν_0 is Rydberg's fundamental frequency for ordinary line spectra I have written it in this form because it is then identical with that which one would expect for the principal line from the theory of Bohr The constant b is equal to 1 Considering the principal line in the L series, the constant b is equal to about 7 6, i e,

$$\nu = \tfrac{5}{36} \nu_0 (N - 7 6)^2$$

Thus for K line
$$A = \left(\frac{1}{1^2} - \frac{1}{2^2}\right) \nu_0,$$

while for the α line
$$A = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \nu_0$$

Of course, one cannot determine the value of A closer than a few per cent., because we saw that the principal line of the L series, when the square root of the frequency was plotted against the number, was not quite a straight line. It is very likely merely a coincidence that the value of A happens to come in that form But I am intending to look for the M series and the N series, and, if they exist, to examine whether they also have constants of this kind. I should like to point out that for the L series the value of b is considerably larger than for the K series The complete difference between the grouping of the lines for the K series and the L series, and the fact that the constant b, which I suppose

to represent the action of the electrons in neutralising the force exerted by the central charge, is very different in the two cases, suggests that the K series corresponds to the vibrations of the inside ring, and the L series to the vibrations of the next ring outside it

This slide is of interest since it shows the spectrum of the specimen of erbium which Sir William Crookes gave me   The α, β, and γ lines are clearly seen, also a line of dysprosium, while the principal line of holmium is just visible It shows how these spectra can be utilised to determine the purity of the specimens

The next slide gives the atomic numbers of all the elements, assuming that we are right in saying that aluminium is No 13   You will notice that the numbers up to 79 have been put in from the evidence of the X-ray spectra After gold, No 79, we assume that the same law continues to hold for the two elements, mercury and thallium, which I have not yet investigated

After thallium we get into the region which Mr Soddy has been studying, and, from the evidence given by him, we can deduce the atomic numbers of all the other radioactive elements up to uranium   You see that there is one more element missing, a homologue of chlorine, and also a homologue of sodium, but it says a good deal for the extraordinary skill and industry of the chemists, that in the whole list there only seem to be five unknown possible elements

Mr F Soddy   I have listened with very great interest to the discussion opened by Sir Ernest Rutherford upon the structure of the atom, and though of course I am not competent to discuss the nuclear atom, if I may give it a name, critically from the mathematical or the physical side, I may say that generally in the broadest way I am in full agreement with that model   I have certainly found it very helpful in my own particular field of work in radioactive investigations   Prof Bragg, more than ten years ago, showed that an α-particle could go through all the atoms it met in its path without suffering any appreciable deflection It is only a particle moving at these ultra-material speeds, speeds which are about one-tenth of the speed of light, such as the α-particle, which can penetrate the atom, and, as the genius of Sir Ernest Rutherford has shown, it may tell us something about what it is that it has passed through   The fact that the law of Bragg is not actually obeyed and that there are these rare single scatterings, to use Sir Ernest Rutherford's term, I think, without any theory whatever, does show that we have to deal with a nebular atom with a hard nucleus   I am not very friendly to the general idea of the electrical theory of matter, but, without any particular assumption as to the nature of the atom, I think that the results of single scattering as shown by Prof Rutherford do undoubtedly prove that we have to deal with a nebular atom which has a hard point in it, a hard scattering point which can deflect a heavy atom travelling at very considerable velocity   I content myself by merely saying that, of course, the electrical theory of matter has now undergone very profound change, because in the Thomson atom there was an attempt made to preserve stability, an attempt which was not altogether successful. But with this new atom we have got beyond any such attempt to preserve stability Because it is perfectly obvious that this nuclear atom, whatever the nature of it may be, cannot obey the ordinary laws of electricity   You could not by any known means concentrate into a space, 10^{-12} cm. in radius, 100 atomic charges of the same

sign   There is no known way of doing it.   You have endowed electricity with the attributes of matter, rather than explained matter in terms of electricity

Passing to my own line of work on this subject, let me briefly describe what led me to the view that there exist in the radioactive series certain elements which had identical chemical properties   It was known before that there were certain radioactive elements, radio lead, for example, which extraordinarily closely resembled other elements, such as ordinary lead   My first practical experience came in connection with meso thorium   The chemical nature of meso-thorium having been kept a technical secret by its discoverer, I had to work it out for myself, and I was amazed to find that, though of a different atomic weight, it yet possessed properties chemically identical with those of radium, and by no known process could you separate those two elements once they were mixed   The work has been carried on by Mr Fleck at Glasgow, who has investigated all the radioactive elements in turn, to see, firstly, whether they resembled any known element, and, secondly, whether they were separable from that element   He showed that every single member of the radioactive series, which has a period of life above a minute, is identical chemically with one or other of the last 12 elements of the periodic table from uranium to thallium   This is a very important point, because you have a new means here of determining a type of complexity of matter which a chemical analysis must necessarily overlook   Suppose that you have a radioactive sequence such as A, B, C, D, E, and F   If we take a common case, A, the primary element, may be chemically identical with D, B with E, and C with F, and by no chemical process would you be able to determine that six elements were present   Chemical analysis will separate three pairs of substances, namely, A and D, B and E, C and F   But if it happens that the periods of average life of the various members of the series are not too long in comparison with the allotted span of three-score years and ten, D, E, and F, in absence of their respective parents, C, D, and E, will disappear with lapse of time   But A will, in time, change into B, B into C, and so on   Hence all six members can be severally distinguished   Radioactivity provides, therefore, a means of distinguishing a complexity among elements in the state of change which is not within the range of chemical analysis   It was in this way that Sir William Ramsay and Hahn discovered radio thorium   Radio thorium, as we know now, is non separable from thorium   In fact, these investigators had separated out meso-thorium from the mineral unwittingly   As meso-thorium was not then known, they naturally assumed that they had separated the radio-thorium from the mineral   We do not know any process at present capable of removing radio-thorium from thorium   They really had separated meso-thorium from the mineral, which, in course of time, changed into radio-thorium

I would like to have my lantern slide *   I showed these results to the Royal Society over a year ago   I need not spend time upon it   It shows the radio-elements arranged in the periodic table according to the chemical results of Fleck and myself, and a great number of other investigators preceding us.   Every vertical row consists of elements occupying the same place in the table, which are not separable from one another by any known process.   Such elements I call isotopes   Two years previously I had shown that the expulsion of an α-particle shifts an element from one place in the periodic table to the next place but one   That

* See ' Chemistry of the Radio-Elements,' Part II, p 3

was followed up by my old student, Mr A S Russell, and at the same time by Herr Fajans in Germany, who supplemented that rule and showed that the expulsion of a β-particle shifts the element one place in the opposite direction Hence the expulsion of one α- and two β particles must necessarily bring the element back again to where it started from, and give you an element completely identical with that which you began with Owing to the existence of inter-mediate members of entirely distinct chemical character you can get the radio-thorium and thorium separately, when by chemical analysis such a thing would be absolutely impossible The result of the experiments of Messrs Russell and Ross, and of Profs Exner and Haschek, of Vienna, is to show that the spectra of these isotopes, as I call them, are very probably identical They showed that it was not possible to get any new spectra lines in a very strong ionium preparation The spectrum was purely that of thorium Although we do not know that the chemical elements are not homogeneous in other parts of the periodic table, the presumption is that they are probably not homogeneous In the last part of the periodic law one has a definite proof that there are 40 elements crowded into the 10 places which are occupied The atomic masses may vary over a considerable number of units from 206, for instance, in the place occupied by the element lead, to 214, 8 units, so there is a possibility that the same occurs in other parts of the periodic table too

Since the expulsion of an α particle with two positive charges corresponds with a shift of two places in one direction, and the expulsion of a β-particle carrying a single negative charge corresponds with a shift of one place in the opposite direction, it follows without any doubt at all that the successive places in the periodic table correspond with unit differences in the *net* value of the nuclear charge, so far as the last 12 places at least are concerned That idea has been followed out further by Mr Moseley, who, I understand, has new results to bring before us to-night

There are a great many problems arising which have not yet been solved It is probable that the ordinary lead of the chemist is not homogeneous If it is derived from radioactive changes it is a mixture There has not yet been time for that point to be decided, but we have been at work on it for some time I regard the discovery of meta-neon and neon in the atmosphere by Sir J J Thomson as a brilliant confirmation of this point of view These two elements, according to the results of Mr. Ashton, appear to differ in atomic weight by 2 units, and yet appear to have the same boiling point and spectrum. They are not capable of separation by fractional condensation in cold charcoal, but are separable by fractional diffusion methods only

The model on the table of the periodic law I think sums up the knowledge we have derived from radioactive changes succinctly * It is based on the figure of-eight spiral arrangement of Sir William Crookes, now over 25 years old, and on the fact that the rate of change of properties in passing from place to place attains a maximum at the zero and a minimum at the eighth group We cannot take the simple symmetrical idea that then sufficed. It illustrates three points which, I think, have to be explained on any theory of the structure of the atom. Firstly, we begin with two simple single turns of the spiral, or short periods. Then at the 22nd element, titanium, the course of the evolution changes and

* See ' Chemistry of the Radio-Elements,' Part II, p 11

gives us the double spiral figure   This proceeds till two complete double turns
have been run through   Then we have a totally different type of evolution
coming in, with the commencement of the rare-earth group   All the elements
are identical in valency, though they differ, of course, from the isotopes which I
spoke of, in that between the successive elements there are distinct, though
exceedingly slight, differences of chemical character, sufficient to enable their
separation by chemical methods to be effected   The sequence then follows on
exactly as though the rare-earth elements had not been interpolated   The final
part between bismuth and uranium is almost all new, but it reproduces in exact
detail the earlier sequence of events   From lead to thorium is the exact analogue
of the early sequence from carbon to silicon

Prof J W NICHOLSON   I think that Prof Rutherford has made it clear that
the nuclear atom is, as a matter of fact, the only basis upon which profitable dis-
cussion of the constitution of the atom can really be carried on   The main
rival theory, as Prof Hicks has just indicated, is the magneton theory   It seems
that just recently in the course of a discussion it has been shown that the magneton
theory and the nuclear theory do probably amount to exactly the same thing
This has been indicated very clearly by Dr Allen, who, I observe, is here to day,
and who, perhaps, may speak about it afterwards   He has shown that the
magneton can be represented as a difference effect which takes place with rotating
electrons, if we suppose that the nucleus is rotating as well, with, however, a
specified angular momentum   The principle of the constancy of angular momentum
gives a possible explanation of Planck's constant, that is to say, if this constant
h is an atomic constant at all, and not a constant of atomic aggregates   It first
came in in connection with the coronal spectrum, which can be represented mathe-
matically by the free vibrations of a very simple model atom in its neutral and
charged configurations   (*Illustrating*)   That is an atom which has a nucleus of
charge 5 and five electrons   This angular momentum principle was taken up by
Dr Bohr and is the real basis, I think, of the success of his theory so far as it
has had success

A hope has been expressed by Prof Rutherford that I would make a few
remarks about Dr Bohr's theory   I have been examining this theory for some
little while , in fact practically ever since it first appeared   There are several
points in which it will work, and others apparently in which it will not work
without very serious modification   In the first place there is the question of the
theory so far as it relates to the more chemical nature of the elements, that is to
say, to the arrangement of the electrons in the atom in a series of concentric
rings of varying radii, the X ray spectra, for example, being supposed to come
from an innermost ring   On the older electrodynamics it is possible to show that
we cannot have, under any circumstances, a set of concentric rings in the same
plane rotating round a single nucleus   It is not possible to satisfy the conditions.
We can have, of course, electrons rotating in other ways than all in the same
circular ring   We can have them all describing ellipses, for example, with the
major axes of those ellipses at equal angles all the way round the nucleus   But
it is not possible to have any approximation to concentric circular orbits on the
old electrodynamics , nor is it possible, as can be proved rigorously—I mean by
strict mathematics —to have them on Dr Bohr's theory, either, in its present form.

On this theory at present the so-called steady configurations of the' atom are to be determined by the ordinary mechanics But it is only when we come to the question of the changes of the atom from one set of stationary states to another, or the vibration of the atom, that the ordinary dynamics must be given up In obtaining the formula of the hydrogen spectrum, Dr Bohr is compelled to suppose that the attraction between an electron and the nucleus in the case of the simple neutral hydrogen atom is according to the ordinary inverse square law which it would follow if the electrons were not actually bound in an atom If we examine what the spectrum of any other atom would be on these premises, that is to say, take any case which Dr Bohr has not taken, we cannot obtain the experimental results But taking first the hydrogen atom in the ordinary neutral state, that particular atom also leads to another spectrum in the extreme ultra-violet, which has recently been found and which agrees very well indeed with the theory In other words, the hydrogen atom certainly does appear to give all the lines that we can get from a certain double series This includes Balmer's formula, Ritz's formula, and a Schumann series

The formula is
$$n = B\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right),$$

where B is Rydberg's constant, and τ_1 and τ_2 can take all integral values

In the case of helium, when there is only one electron approaching the atom, we get the same series with half instead of whole numbers, and one immediate deduction, among others, is that the entire hydrogen spectrum is also given by the helium atom when it has a positive charge

Actually there is a slight correction to be made in B, because when you have only one electron, it drags the positive charge out of its ordinary position The two series for hydrogen and helium are not really quite the same, but they are very nearly

If we take the same premises and try to get the rest of the helium spectrum— that is to say, the ordinary helium spectrum—the attempt fails altogether We get other series of this kind if we work out the varying stages according to the theory given by Dr Bohr If we try to get the spectrum of a charged hydrogen atom or a hydrogen molecule, the same thing takes place We can get nothing approaching the facts at all, and we must bear in mind that we have an entire secondary spectrum of hydrogen, or what is now generally believed to be due to hydrogen, with about 400 lines, which has yet to receive explanation by any theory of the structure of the hydrogen atom, in addition to those theories which have been mentioned

I have examined in what direction we can modify this theory in order to get such spectra I find that there are two ways We can either make a different specification of the angular momentum—but that is not sufficient in itself—or we must suppose that, although the electron and the nucleus exert the usual force on each other, electrons bound in an atom must not exert the same force on each other as they normally do I think that, in dealing with a subject like this, we are, perhaps, entitled to make any tentative assumption we like, which leads to an experimental formula, in order to endeavour to throw some light on the subject. I find, however, that no inverse law of any kind will lead to anything approximating to the ordinary spectrum of helium at all The only way in which any progress seems likely in connection with ordinary spectra is to suppose either

that there is no force whatever between electrons bound in an atom, or that it is according to some power which is not an inverse power.

When we come to the X-ray spectra some very interesting results appear

The first point that I wish to emphasize is in relation to the ordinary deduction first given by Mr Moseley, that Bohr's theory is in agreement with his results on the X-ray spectra

When we examine Bohr's spectral formula, we get

$$V = Bn\,(N - b)^2 \left(\frac{1}{\tau_1{}^2} - \frac{1}{\tau_2{}^2}\right)$$

b is a constant depending on the number of electrons, that is to say, in addition to that factor in $(N - b)^2$, the factor n comes in   This has been overlooked in the treatment of the question so far   There is only one way of removing n, and that is to give up one of Dr Bohr's fundamental postulates, which is to the effect that when radiation is given from an atom only one quantum must go at a time   If there are n electrons, we must suppose that every one of those electrons sends out a quantum   If we do this, we can get the n on the other side of the equation, and it may be cancelled   That is the first proviso we must make if we want the X ray spectra to fit in with the theory

If Mr Moseley's rings are impossible, then his supposed ring of four electrons round the nucleus will have to go too, except in one circumstance, namely, that there is no force between the bound electrons in the atom   If there is no force in the bound electrons in the atom, then we can proceed a little farther   The constant b disappears   We get the frequencies of the X-ray spectrum proportional to the square of N   (*Illustrating*)   Mr Moseley's results do indicate so closely this proportionality to a square that I think it would, perhaps, be better to accept it as a fact rather than suppose that there is a constant b concerned there which happens to be equal to 1 in the case of calcium and some of the other elements   Here, however, we have the difficulty that if N represents the atomic number the N for calcium comes down to 19, that is to say that if the theory of the atomic number being equal to the place of the elements in the table is correct the chemists have not found exactly the right number of elements between hydrogen and calcium, but have found one too many   However, I do not want to dwell on that point now If this absence of force between bound electrons is a fact, isotopes will have the same spectrum

There is one other point on which I would like to make one or two remarks   I referred to the question of the coronal spectrum, which can be explained by the vibrations of an atom consisting of a nucleus of $5\,e$, and 5 electrons   This atom I do not take to be an ordinary terrestrial atom of similar constitution   I take it to be an atom with a simple nucleus   I think that the nature of the binding of the electrons to the nucleus must indicate some change in it from the form of a terrestrial atom   If we examine the spectra of nebulæ in the same way, we get the same result with respect to a system of four electrons outside a nucleus of four   We can explain a large part of the nebular spectrum in this way Recently I think I have managed to show that we can explain practically all the radiations of nebulæ by the other systems of this simple kind , that is to say, we have the very beginnings of matter there , and the subsequent development of terrestrial matter will have to take place by some modification of the interior of

the atoms The evidence for this modification is, that when we come to the stars which astronomers regard usually as the earliest type of stars, namely, the stars close to the nebulæ in stellar classifications, we find that they contain no lines which can be certainly identified except hydrogen and helium lines. They contain, however, about forty lines which can all be grouped together under one comprehensive formula which is exactly like Balmer's formula, except that the constant 4 is replaced by something else, and there is a series of limits with a constant frequency difference outside The constants in these formulæ are certain constants we can calculate for the original system in the nebulæ with the four electrons and the nucleus of four which seems to be the recognised system there There is evidently some relation between the origin of those lines and the origin of the lines in the nebulæ Moreover, if we trace through exactly the same relation for the subsequent products of another atom—that is to say, the atom with a simple nucleus (whatever that may be) and one electron—we get exactly Balmer's formula We get the limit right We get it right to five figures on the supposition that this explanation of the nebular spectrum is correct Apparently therefore hydrogen does contain only one electron Moreover, if we make the same calculation for an atom with two electrons we get *this* as the chief line (*Illustrating*) I do not deny that there are probably other series We get the wave-length 10832 as the principal line, and the strongest line in the helium spectrum is 10830 I think that from this empirical method of proceeding there is very strong evidence that the supposition that hydrogen has a nucleus of 1 and helium of 2 is correct If we go any farther the same thing does not happen We cannot show in the same way that the nucleus of lithium has a charge of 3

There is one little difficulty which I may, perhaps, refer to as regards the spectra Prof Strutt recently has indicated some experiments which seem to support a view expressed by Lenard some little while ago that the systems whose vibrations give the principal series and the subordinate series are different Lenard's view was that the principal series came from neutral atoms and that the subordinate series came from the various positively charged atoms If helium has only two electrons we cannot expect a spectrum when no electrons are left at all In that case the subordinate series of helium must be the spectrum of the atom which, according to Dr Bohr's theory, gives us what are called by astronomers the Pickering lines The line 10830, of the principal series, by our method appears to be in agreement with Lenard's view, for it comes from a neutral atom There will be these points ultimately to be reconciled between Dr Bohr's view and this more empirical view which I have ventured to bring before you

Prof W M Hicks As there is not time to say very much, I will go at once to the one or two points that I wish specially to draw attention to The first is in reference to Mr Soddy's theory of the existence of elements having different atomic weights, and yet having the same chemical properties I think that we shall all agree that the evidence in favour of that is so strong that we may take it as practically, or at any rate provisionally, settled ; but a difficulty arises in connection with the spectra He assumes that the spectra of these different substances with different atomic weights, but belonging to the same place, will be identical. Certainly in favour of that view the result of the attempt to

determine the spectrum of ionium seems to lend some weight, but there is a difficulty which it seems to me we cannot get over, namely, that the spectra of the elements depend very definitely on the atomic weight and not on the number It is not simply a rough connection. It is a connection so close that if you take the atomic weight to be 1 or 2 in 3000 different from the weight as determined by chemists, then the relation falls out altogether Here we have cases where the atomic weight differs by 3 or 4 units It is difficult to see how you can expect to get the same spectra. An explanation may lie in the possibility that we never have the single element in these cases, so that, for instance, in the spectrum of thorium we do not get the spectrum of pure thorium, but that of a mixture of thorium and ionium and all their isotopes together All these elements have an enormous number of lines, and their spectra have none of them been properly investigated, so we do not know whether we have a mixture of the spectra of several isotopes when we take, say, the spectrum of thorium, or not

Of course there is another supposition that we might take, namely, that the isotope with the largest number of electrons is the one which gives the ordinary spectrum, and that these other elements which are brought back by the emission of β-rays have no spectra at all But it seems to me that the most likely thing and the thing that we have to look for is that the observed spectra are really composite.

The other point which I wanted to raise was one of a different kind If we approach the constitution of the atom from the spectral side we are led to think more of the magnetic qualities of the atom than of the electrical You must have magnetic fields, in anything which produces ordinary spectra, at least those which show spectral series This has been pointed out by Lord Rayleigh and has been applied with great success by Ritz Not only so, but we know from Weiss's experimental work that these little atomic magnets do really exist Whether they are something different from electrons, or are produced by rotating electrons, is a matter for further consideration, but the fields are so strong that they must be taken into account The measured amount of their magnetic moments is of the order 10^{-21} Although the mathematical difficulties may be great, I think that if the theory of the deflection of an α-particle by one of these magnetons were worked out it would be found that deflections quite comparable to those observed would be found, and that too by particles which do not require to go so close to the central nucleus as in Prof Rutherford's theory ; but of course whether the law of scattering is the same as what he has observed or not, we do not know That is a matter in which the mathematical theory would have to come first Some rough calculations I have made show that α- or β-particles passing in the equatorial plane of a Weiss atomic magnet do, as a fact, get scattered in all directions by such an amount as to lead to an expectation that the law would be similar to that which Prof Rutherford has observed.

Prof SILVANUS P THOMPSON May I be allowed to put a point ? Prof Hicks has referred to a feature which apparently has escaped the attention of almost all the older workers on this subject, namely, that there must be magnetic force in these hypothetical atoms, if they consist of electrons in motion He has referred also to the brilliant work done by Prof Weiss in his investigation of the possible

atomic magnet or *magneton* It is worth while to put that from another point of view, or rather to show one of the additional complications that this consideration introduces. What Prof Weiss has done is this —Taking various magnetic substances, and magnetising them in the strongest possible field, so as to produce as near an approach as possible to magnetic saturation, he has found that there is apparently a definite magnetic moment for the atom of each of these. Putting it into the usual quantity of gramme molecules, 56 grm of iron appear to have, in the limit when they are magnetised completely, a magnetic moment of 12360 (C G S. units), 59 grm of nickel, the corresponding quantity, appear to have 3370 units of magnetic moment Those two numbers have, as Weiss points out, exactly the relation numerically to one another of 11 to 3 If you take 59 grm of cobalt in the same way and express its magnetic moment in the same terms, the unitary number that corresponds to it is 9 If you take 16 grm. of oxygen, the corresponding number is 7 That is to say, the atoms respectively of iron, nickel, cobalt, and oxygen contain these numbers of magnetons iron, 11 (or, in other circumstances, β-iron apparently will contain 12), nickel 3, cobalt 9, and oxygen 7 Now, what I want to point out is this —If we accept the argument of Weiss on this point, we must consider the atom not only as a nucleus with a certain electric positive charge in it, and electrons, negative units, grouped around in rings or some other configuration, but its configuration must be such as to have these elementary quantities 11, 3, 9, 7 for the four elements in question Arrangements have been proposed of models of atoms having so many units of positive electricity grouped with so many electrons of negative electricity Have we there any basis whatever for supposing that these unitary magnetic numbers can be accommodated therein? Our model atom of oxygen, however many positive and negative aggregate units it is supposed to have, must possess a configuration such that it shall have seven magnetic units in it This is a somewhat novel point of view, but apparently it is a necessity from the facts It adds, no doubt, to the difficulties of imagining a model that will work, but a model that will not work magnetically, but only mechanically, is only half a model

Dr. H. S ALLEN. Like Prof. Hicks I have been trying recently to work out the question of the scattering of the α-particles by a magnetic atom I find, however, that there is one point of difference between the electric and the magnetic problem, which I think is crucial. In the case of the nucleus Sir Ernest Rutherford has shown that the scattering varies inversely as the fourth power of the velocity. Taking the magnetic atom and dealing with the case in the equatorial plane, I think that the scattering varies inversely as the square of the velocity So there is this important point by which we may distinguish between the two views I am not quite sure whether the experimental evidence obtained so far is really decisive. I think that if we were to take a magnetic atom which also possesses electrical properties we might find a relation somewhere between the square and the fourth power which possibly might fit the experimental facts more closely

With regard to magnetons, I want to mention one point very briefly. We may express the angular momentum of an electron as $ma^2\omega$, supposing that we have an electron travelling in a circular orbit of radius a, with angular velocity ω. According to Bohr's theory the angular momentum is equal to $h/2\pi$ The magnetic moment of an elementary magnet, which would be equivalent to the revolving

electron, is equal to $\frac{1}{2}ea^2\omega$ Comparing these two, we see that it is possible to express the magnetic moment in terms of Planck's constant h. If we work out the result, using the latest value for the constants, we find for the magnetic moment the value $92\ 7 \times 10^{-22}$ Now, taking the latest value for the magnetic moment of the magneton we get the number $18\ 54 \times 10^{-22}$. The former number, then, is *exactly* five times the latter, that is to say, the single electron revolving in a circular orbit is equivalent to five magnetons That was pointed out first by Mr. Chalmers at the recent meeting of the British Association. In order to arrive at the magneton itself, I suggested in a letter to 'Nature,' a few weeks ago, that we might take the case of a revolving sphere of positive electricity. It is easy to show that, if we have a sphere carrying a charge N times e, the magnetic moment of the revolving sphere is $\frac{1}{5}NeA^2\Omega$, where A is the radius of the sphere and Ω its angular velocity If we assume that $A^2\Omega$ is equal to $a^2\omega$, the magnetic moment is equivalent to 2N magnetons , so that, by taking $5n$ magnetons for the ring of n electrons and 2N magnetons for the revolving sphere, we have a way of building up various numbers of magnetons according to the direction of revolution of the sphere and the ring Prof Rutherford, I suppose, would prefer to make the sphere of negative electricity and put a positive nucleus in the centre In that way we might be able to reconcile the two points of view

Reply of SIR ERNEST RUTHERFORD —As the hour is so late I will only delay you for a few minutes I must first of all thank the speakers for the kind way in which they have treated me in this discussion, and I think there are not many points which call for a special reply

I quite recognise, with Prof Hicks, that there must be an atomic weight term connected with the frequencies of vibration of the atom On the theory I have outlined, it is to be anticipated that this term should be very small, and it is difficult to account for the magnitude of the effect observed experimentally by him In making the statement that elements of the same nucleus charge should have the same spectra, I am quite aware that this can be only approximately the case There should always be a small difference in the frequency of vibration due to the mass of the nucleus, and no doubt the magnitude of this term will depend upon the relative masses of the two atoms, which have the same nucleus charge According to our present views, however, this effect should be very small, and for a heavy atom should not amount to more than 1/100 of an Ångström unit. In my remarks I did not discuss at all the very thorny question of the outer distribution of electrons There is no doubt that in a heavy atom this distribution is very complex and will be difficult to calculate with certainty

I am very glad that Prof Nicholson has given us his views on the origin of the spectra, and was very interested in his discussion of how far the theories of Bohr are applicable, and how the results given by Mr Moseley can be interpreted. Even supposing that our fundamental assumptions are right about the nucleus and the importance of the nucleus charge, I think it will be some time before we shall be able to enter with any detail into the very complicated question of the electronic distribution of a heavy atom There are so many possible modes of arrangement of the electrons, and there is always the uncertainty that we do not know completely the laws which govern the influence of one electron on another. Obviously very many possibilities will have to be considered before we can hope to obtain a

satisfactory explanation. Any structure which is assumed must explain not only the general chemical and physical properties and the spectra of the elements, but also the magnetic properties of the atom,* to which I am glad attention has been directed by Prof Silvanus Thompson and Dr Allen

I am afraid that I have already taken up too much of your time in this discussion I personally take a very great interest in this subject, and to-day I have tried to give you briefly my general views and the theories on which many of us are working to-day I am glad that we have had such an interchange of views on some of the main problems of atomic structure, and that there is comparatively so much agreement in regard to the central point of the atom

<div align="right">E R</div>

* [*Added June* 19, 1914 —It must be borne in mind that the magnetism of iron and nickel are very much affected by their physical and chemical state and their combination with other substances It thus appears probable that the intense magnetic effects of iron and nickel are in some way connected with the arrangement and motion of the electrons near the surface of the atom, and are only indirectly connected with the interior structure of the atom —E R]

The Relation between the Crystal Symmetry of the Simpler
Organic Compounds and their Molecular Constitution.—
Part III.

By WALTER WAHL, Ph.D.

Theoretical Part

The investigation of the crystalline properties of the simpler organic
bodies, gaseous or liquid at ordinary temperature, has been described in
Parts I and II * In this paper the experimental results will be discussed
with regard to their bearing upon the problem of the relationship between
molecular constitution and crystal symmetry.

In order to facilitate a comparison the experimental results are summarised
in the table on p 2.

As seen from the table, more than 50 per cent of the substances
investigated are polymorphic, and to this class nearly all the substances
which contain only one carbon atom belong   The question therefore arises
which one of the crystalline modifications of a substance is to be compared
with the one or the other form of another substance, or with the crystals
of a substance of which only one modification is known   In most of the
cases investigated very little is known with regard to the modification stable
at low temperature, and thus for practical reasons only the form crystal-
lising directly out of the liquid state can be taken into account.   Also, from

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 354 (1913) , and vol. 89, p. 327 (1913).

Substance	Crystal-form on crystallisation from the liquid state	Polymorphism
CH₄	Cubic	Dimorphic e*
CH₃Cl	Orthorhombic or monoclinic	—
CH₂Cl₂	Orthorhombic	Dimorphic e
CHCl₃	Hexagonal†	—
CCl₄	Cubic	Dimorphic e
CH₃Br	Monoclinic	Trimorphic e
CH₂Br₂	Orthorhombic	Dimorphic e
CHBr₃	Hexagonal	Dimorphic e
CBr₄	Cubic	Dimorphic e
CH₃I	Monoclinic	—
CH₂I₂	Orthorhombic	Tetramorphic e‡
CHI₃	Hexagonal	(Dimorphic?)
CI₄	Cubic	—
CH₃(NO₂)	Monoclinic	—
C(NO₂)₄	Cubic	Dimorphic e
CCl₃(NO₂)	Tetragonal, hexagonal, or orthorhombic	Dimorphic e
CO	Cubic	—
CO₂	„	—
CS₂	Monoclinic or triclinic	-
COS	Tetragonal, hexagonal, or orthorhombic	—
COCl₂	Tetragonal or hexagonal	Dimorphic m
CH₃.CH₃	Hexagonal	—
CH₃ CH₃	Monoclinic	—
CH' OH	Cubic	Dimorphic e
CH₃.CH₂.CH₃	Orthorhombic or monoclinic	Dimorphic e
CH(CH₃)₃	Hexagonal	
CH₃ CH₂ CH₂ CH₃	„	Dimorphic e
CH₃ (CH₂)₃ CH₃	Orthorhombic or monoclinic	—
CH₃(CH₂)₄.CH₃	Monoclinic or triclinic	—
CH₃.(CH₂)₅ CH₃	„ „	—
CH₃ (CH₂)₆ CH₃	„ „	—
C(CH₃)₄	Cubic	Dimorphic e
CH₃ OH	Monoclinic or triclinic	Dimorphic e
C₂H₅.OH	Orthorhombic, monoclinic, or triclinic	
C(OH)₃ OH	Hexagonal	Dimorphic e
CH₃ O CH₃	Orthorhombic	—
CH₃ O C₂H₅	Monoclinic or triclinic	—
C₂H₄ O C₂H₄	Orthorhombic	Dimorphic m
CH₃ CO CH₃	Monoclinic or triclinic	—
C(O CH₂ CH₃)₄	Tetragonal (pseudocubic)	—
C(CH₂ OH)₄	Tetragonal	—
CH₂ CH₂.OH₂	Hexagonal	—
CH₂.CH₂.CH₂.CH₂.CH₂ CH₂	Cubic	Dimorphic e
CH₂ CH₂ CH₂ CH₂ CH₂.CH CH₃	Monoclinic	—
C₆H₆	Orthorhombic	—
C₆H₅ CH₃	„	—
1.4-C₆H₄ (CH₃)₂	Monoclinic	—
1 3 5 C₆H₃(CH₃)₃	Orthorhombic	Dimorphic m
C₆(CH₃)₆	„	—
C₆Cl₆	„	—
C(C₆H₅)₄	„	—

* e = enantiotropic , m = monotropic
† Hexagonal includes trigonal
‡ According to Tammann and Hollmann

a theoretical point of view, it seems that, in a comparison between the molecular structure and crystal form of a body, the modification which crystallises directly out of the liquid state or, in cases of monotropy, the modification of higher melting point, which is the stable form, should in the first place be taken into account, as it seems probable that the crystalline modification in equilibrium with the liquid at the melting point corresponds to the molecules predominant in the liquid and gaseous states

In most cases where the complete crystallographic investigation of a substance is given in the literature the crystals investigated have been obtained by crystallisation from solution, either at room temperature or at a temperature only slightly higher. The crystals investigated are therefore often not those which are obtained directly from the liquid state, but correspond to another crystalline modification An instance of considerable importance may serve to illustrate this Carbon tetrabromide is given in Groth's handbook as being monoclinic, since the crystals obtained at room temperature from solutions are monoclinic On heating, these crystals change into a regular form at $+46°$, and the regular form melts at ordinary pressures at $92.5°$ Therefore in the table given here carbon tetrabromide is mentioned as regular, but dimorphic Cases like this are numerous, and, in order to enable comparisons to be made, all substances which are quoted in this paper have been investigated optically at a temperature immediately below the melting point, with a view to ascertaining whether the modification described in the literature is the one formed directly out of the liquid condition, or whether it is another polymorphic modification

In the first series of results published on the investigations of bodies gaseous or liquid at ordinary temperatures, it has been briefly pointed out with regard to the optical method of determining the crystal system of a body that it is, of course, not in all cases possible to determine by such a method to what crystal system a body belongs, as the crystals of some substances incline to grow only in certain crystallographic directions It will be noticed from the summary of the experimental results that it has, as a matter of fact, not been possible to determine in some instances to which crystal system a body does belong, but that two or three alternatives are given It seems, therefore, fitting at this stage to point out that the crystal-optical method, although it gives results which in most cases render the exact determination of the crystal system of a body possible, and also gives valuable information about the general properties in the solid state of substances gaseous or liquid at ordinary temperature, is not intended to replace an ordinary crystallographic investigation, but to be used in cases which hitherto have been entirely inaccessible to crystallographic research,

although from the point of view of general chemistry they are of great importance. The experimental results of this investigation and the theoretical conclusions drawn from them have to be judged from this point of view.

Discussion of Results

(a) *Compounds containing One Carbon Atom.*—In order to facilitate discussion the compounds containing one carbon atom will be dealt with first, and the substances containing several carbon atoms will then be considered In view of the tetravalency of carbon, methane may be regarded as the parent substance from which all the other carbon compounds may be derived by substitution of the hydrogen atoms The tetra-substitution products of methane, in which all the substituents are equal among themselves, may further be regarded as being equivalent with methane from the point of view of the architecture of the molecule The question therefore at once arises whether to this highest degree of symmetry of the chemical molecule there corresponds a crystal form of high symmetry, irrespective of the nature of the atoms attached to the carbon atom, or whether the character of the four atoms attached to the carbon atom determines the crystal form of the compound This is, of course, only a special instance of the general question whether the crystal form is an "additive" property depending on the specific properties of each constituent which makes up the compound, or whether the crystal form is a "constitutive" property, depending not on the specific properties of the constituents but on the constitution of the compound

Carbon itself is known in two crystalline modifications, diamond and graphite, the one regular, the other hexagonal. In the carbon tetra-compounds, methane, carbon tetrachloride, carbon tetrabromide, carbon tetra-iodide, tetranitro-methane, and tetramethyl-methane, the carbon atom is associated with hydrogen, which in the elementary state crystallises in the regular crystal system,[*] with chlorine which is orthorhombic,[†] with bromine which is orthorhombic,[‡] with iodine which is orthorhombic, but which has besides been observed to occur in a monoclinic modification, and lastly with the —NO_2 and —CH_3 groups, of the eventual specific crystalline properties of which nothing can be said All these compounds have been proved to crystallise as regular crystals out of the liquid state If the specific crystallographic properties of the atoms as they appear in the elementary state—

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[*] 'Roy. Soc. Proc.,' A, vol. 88, p. 64 (1913)
[†] 'Roy. Soc. Proc.,' A, vol. 88, p. 350 (1913).
[‡] 'Roy. Soc. Proc.,' A, vol 88, p. 352 (1913).

or, more correctly, the forces which act to make an element crystallise in a certain manner—would also determine the crystal system of the compounds of this element, we should expect that out of the above compounds only methane would be regular, but that on the other hand carbon tetrachloride, as being built up out of one atom which in the elementary state is regular, and four atoms which in the elementary state are orthorhombic, would show a less degree of symmetry and be rhombic or possibly tetragonal From the fact here established that all these compounds crystallise in the regular crystal system, the conclusion must be drawn, that the specific crystal form of an element does not determine the crystal form of its compounds, that is that

The crystal form is not an additive property of matter

The same conclusion may also be drawn from the circumstances that the oxides of carbon and several other oxides are regular, although oxygen, as has recently been found,* does not crystallise in the regular crystal system

The above does not imply that the properties of the atoms themselves as manifested in their crystalline form in the elementary state, or the forces which cause them to crystallise in a certain form in the elementary state, have no influence at all upon the crystal angles or the crystal form of the compounds On the contrary, it seems almost certain that this is to some extent the case, at least in a secondary way

We may proceed to discuss the mono-, di-, and tri-substitution products, in which the substituents are identical among themselves, on the assumption that the crystal form is a constitutive property The mono-substitution products CH_3Br, CH_3I, CH_3NO_3, have been found to be monoclinic, CH_3Cl rhombic or monoclinic, and $CH_3.OH$ monoclinic or triclinic The di-substitution products CH_2Cl_2, CH_2Br_2, CH_2I_2, have been found to be orthorhombic; the tri-substitution products $CHCl_3$, $CHBr_3$, CHI_3, hexagonal Di- and trinitro-methane have on account of their instability not been investigated No other di- and tri-substitution products of methane which do not contain larger groups than the methane nucleus itself are available for comparison

We thus observe that when one hydrogen atom in the regularly crystallising methane is substituted by some other univalent atom or group, the resulting compound crystallises in one of the crystal systems of comparatively low symmetry. By such a substitution the symmetrically built molecule of methane, consisting of one carbon atom with four hydrogen atoms grouped around it, is changed into a highly unsymmetrical molecule in which the

* 'Roy Soc Proc.,' A, vol. 88, p 65 (1913).

carbon atom is surrounded in three directions of space by three hydrogen atoms and in the fourth by a much larger atom or group If, then, one more hydrogen atom is substituted by an atom 'or ,group identical with the first substituent, the contrast in the molecule produced by the introduction of the first substituent becomes diminished, the molecule in this case consisting of a carbon atom surrounded by two pairs of atoms identical between themselves As a result the crystal form of these di-substitution products shows a higher degree of symmetry, being orthorhombic, than that of the, mostly monoclinic, mono-substitution products. By introducing a third substituent, the symmetry of the molecule is further increased, as it now consists of the central carbon atom surrounded by three large atoms, which are identical between themselves, and the remaining hydrogen atom The predominance of the three substituents manifests itself in the hexagonal crystal form of these bodies If then the last hydrogen atom is similarly substituted, we obtain the tetra-substitution product with a symmetrically built molecule similar to methane itself All these tetra-substitution products crystallise in the regular system similarly to methane The crystal system of the substitution products of methane is thus entirely dependent upon the symmetry of the chemical molecule itself, and all the changes in the symmetry of the molecule which take place as a result of a substitution in the molecule of one univalent atom or group by another, are reproduced by a corresponding change in crystal symmetry The conclusion may therefore be drawn that

The crystal symmetry of the simple carbon compound is a constitutive property, which is determined by the symmetry conditions of its chemical molecule

The remaining one-carbon-atom compounds contain the divalent atoms O or S. The atoms of these molecules lie in one plane, and it is not possible to speak of a greater or less degree of symmetry in the build of such molecules as they are in themselves of so simple a constitution It is therefore not surprising that molecules like CO and CO_2 crystallise in the regular system. It might be expected that CS_2 should crystallise in a similar way to CO_2, but this is not the case, the CS_2 crystals possessing a low degree of symmetry COS again stands intermediate between CO_2 and CS_2 with regard to its crystal symmetry. $COCl_2$, however, is not intermediate between CO_2 and CCl_4, as these are both regular while $COCl_2$ is tetragonal or hexagonal.

(b) *General Considerations regarding the Properties and the Symmetry of the Chemical Molecule*—In the above discussion of the relationship between the molecular symmetry and the crystal symmetry of the one-carbon-atom compounds, the chemical molecules have been dealt with as structures capable of

possessing a definite degree of symmetry * This does of course not imply that the atoms are thought to occupy an absolutely fixed position in a kind of rigid structure forming the molecule. In order to be able to assign to a molecule a definite degree of symmetry, it is sufficient to assume, firstly, that the atoms inside the molecule are attached to the central carbon atom and drawn to this by the four valency forces of the carbon atom acting in conjunction with the valency forces of the atoms attached to it, and secondly, that the atom of each element occupies a certain definite amount of space within the molecule, which space may be styled—using a term already used in a similar sense by Barlow and Pope† and by Richards‡—the "atomic sphere of influence" In this way is produced an assemblage of atoms, or atomic spheres of influence, packed as closely to each other as possible The questions as to how the atom itself is built up and of whether the material mass of it occupies the entire space of the sphere of influence or not, or whether the material mass is in motion or remains motionless inside the sphere of influence, are immaterial to the present discussion of the symmetry of the chemical molecule It might, however, be pointed out briefly that, from the point of view of the corpuscular theory,§ it is not improbable that the atoms themselves remain comparatively at rest, relative to each other, inside the molecule which vibrates as a whole We must assume that the electrons of which the atoms are built up, according to this theory, are involved in strong rotation, and that this rapid rotation of the electrons acts gyroscopically, giving stability to the position of the atoms From such a conception of the build of the atom follows a comparatively stable mutual arrangement of the atoms inside the molecule

There is further the question of the crystal molecules to be considered. In crystallography a distinction is often made between the chemical molecule and the "crystal-molecule," which is supposed to be composed of a great number of chemical molecules. No experimental proof exists as to the existence of such "crystal-molecules" or as to their size measured in numbers of chemical molecules However, if such "crystal-molecules" exist, the discussion in this paper would not be in any way influenced

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* With regard to earlier discussions on the symmetry of chemical molecules, compare Le Bel, 'Bull. Soc. Chim' (3), vol. 3, p. 790

† Barlow and Pope, 'Chem. Soc. Journ.,' vol 89, p. 1675 (1906), and vol 91, p. 1150 (1907).

‡ Richards, 'Zeitschr. Phys. Chem.,' vol 40, pp 169 and 597 (1902).

§ Compare J J Thomson, "The Structure of the Atom," 'Phil Mag,' 1904, p 237. Nagaoka, 'Phil Mag,' 1904, p. 445 , J W Nicholson, 'Month Not. Roy. Astro Soc,' vol. 72, p. 49 (1912) ; E. Rutherford, 'Phil. Mag.,' May, 1911, p 669, and October, 1912, p. 461.

thereby, since the "crystal-molecules" must be thought of as being small crystal units of the fully developed crystal itself, and consequently as belonging to the same crystal system as this All that applies to the relationship between the chemical molecule and the crystal form of the compound would therefore also be applicable to the relationship between the chemical molecule and the "crystal-molecule"

In the preceding discussion on the compounds containing one carbon atom the symmetry of the chemical molecule has been dealt with in a quite general way The symmetry of a molecule may, however, be defined more precisely by adopting the definitions of symmetry which have been developed in the study of crystals * If we now consider the carbon compounds containing only one carbon atom, which have been investigated here from the point of view of the kind of symmetry-elements by which they are characterised, we observe that methane, CCl_4, CBr_4, and CI_4, represent what we may call the tetrahedral case of symmetry, the molecule containing four three-fold and three two-fold axes of symmetry, and six planes of symmetry A crystal of the corresponding degree of symmetry belongs to the regular system, in which the above substances accordingly have been found to crystallise The molecule of a compound like $C(NO_3)_4$ will be characterised by the same elements of symmetry as CH_4, since the three atoms in the nitro-group must lie in a single plane, and will therefore not alter the symmetry of the molecule when introduced instead of H or the halogens That this body CN_4O_8 crystallises in the regular system is therefore of considerable interest

In a tetra-substitution product of the type CR_4, each of the four substituents occupies an equal amount of space, and whether the total amount of space jointly occupied by the four substituents is the same as that occupied by the four hydrogen atoms in methane or not, or whether the sphere of influence of the central carbon atom is altered on account of the mutual forces attracting the atoms to each other (the valency forces), or on account of the close packing of the atomic spheres of influence, or not, the symmetry of the molecule remains the same But if a substituent X of different nature is introduced the question arises, whether this occupies an amount of space different from that of R (*i.e*, a different atomic volume) or not, and whether the specific properties of the sphere of influence of X will in some respect alter the spheres of influence of the carbon atom and of the three remaining atoms R. Supposing that the

* The definition of the symmetry laws and the terminology of the symmetry elements, as given in Groth's 'Physikalische Kristallographie,' will be followed here.

substituent occupies the same amount of space, then clearly the symmetry would not be altered in any way, and in consequence we might expect to find all the simple substitution products of methane regular, as is methane itself and its tetra-substitution products of the type CR_4. This is, however, not the case, and we must therefore conclude that a substituent X introduced into the molecule will either not necessarily occupy the same amount of space as R, or that it will affect in some way the sphere of influence of the carbon atom.

If the substituent X only occupies a different amount of space, but does not alter the sphere of influence of the carbon atom, then all such substitution products, CR_3X, would possess a molecule of trigonal symmetry,* and we might expect these substitution products to crystallise in the trigonal (or hexagonal) system, and to differ from each other principally in the ratio between their principal axis and their lateral axes   If, however, the substituent affects the sphere of influence of the carbon atom, on account of the mutual attraction between these atoms, the sphere of influence of the carbon atom and probably also that of the substituent itself will be deformed, as a result of which the valency direction C—X may be altered as compared with the corresponding valency direction in the molecule CR_4 The molecule of the substitution product CR_3X will in such an event possess only one plane of symmetry but no axes of symmetry, and we may expect such a body to crystallise in the monoclinic system.

Now the experimental results show that the substitution products of methane of the type CH_3R are, as a rule, monoclinic, whereas the substitution products of the type CHR_3 are hexagonal (or trigonal)   That is, when the atomic volume of the group X in CR_3X is large compared with that of R (R in this case $=$ H) and of C, such a distortion of the direction of the valency-force C—X takes place, but when the atomic volume of the group X is small compared with that of R (R in this case $=$ Cl, Br, I) no distortion of the valency direction C—X manifests itself in the crystalline form of the substitution products

From the difference in crystal form of the mono-substituents examined from that of the tri-substituents, we thus arrive at the conclusion that .

> the properties (mass) of the four atomic spheres of influence connected with the carbon atom influence, to some extent, the sphere of influence of the carbon atom, whereby the symmetry of the molecule may be affected. The specific properties of the atoms connected with the carbon atom thus indirectly influence the crystal form of the body

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* One trigonal axis of symmetry passing through C and X, and three planes of symmetry passing through this axis.

If we then turn to the di-substitution products, we again find that if the substituents X in a body CR_2X_2 occupy the same amount of space as the atoms R, and do not influence the sphere of influence of the carbon atom in a different way from R, then such a di-substitution product ought to be regular If, however, the volumes occupied by R and by X are different, or if the effect on the atomic sphere of influence of the central carbon atom is of a different order, the molecule CR_2X_2 will show orthorhombic symmetry, and possess a two-fold axis of symmetry and two planes of symmetry which pass through the axis, but which differ one from the other This is what actually takes place, the di-substitution products investigated have all been found to be orthorhombic

The conclusions we arrive at as to the mutual influence of the " sphere of influence" of the different atoms upon each other are not surprising, from the point of view of the theory of the compressibility of the atoms which has been put forward by Richards,[*] and which has been shown by him to explain in a satisfactory way so many of the phenomena connected with the properties of the atoms [†] In fact, the results given here may be regarded as forming a further proof of the value of the theory of compressible atoms as applied to the study of crystalline form, a value which has recently been pointed out by Richards in a paper on "The Chemical Significance of Crystalline Form"[‡] In all the examples of bodies of the type CR_3X studied here, the difference between the atomic volume of any of the substituents and that of hydrogen is very large, all the substituents also having a larger atomic volume than the carbon atom There are, however, at present, not sufficient experimental results available to permit of the question being answered as to whether the bulk of an atom, in itself, is sufficient to cause a deflection of the direction in which the valency force of the carbon atom acts from the direction in a regular tetrahedron, or whether the specific properties (build, shape) of the atom are the real cause of this deflection § Since the compressibility of the

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    * Th W Richards, 'Zeitschr Phys Chem ,' vol 40, pp 169 and 597 (1902)

    † Th W Richards, " Faraday Lecture," 'Chem. Soc Journ,' vol 99, p 1201 (1911).

    ‡ Th W Richards, 'Amer Chem Soc Journ ,' 1913, p. 381

    § It may also be pointed out that the crystal systems are not separated from each other in any very distinct way, but that forms which show a "pseudo-symmetry" of a higher system often occur There are forms which keep a kind of intermediate position between several other forms, and a small distortion in one or the other respect therefore in such cases is sufficient to bring about a change to either a higher or a lower degree of symmetry The case of a trigonal pyramid is of special interest, and may therefore be quoted as an example a slight distortion in one direction may lead either to a regular, an orthorhombic, or a monoclinic symmetry In large molecules especially we must expect that alterations in the crystal symmetry may take place, for example, when a

elements, as Richards has shown, is a periodic function, just as the atomic volume is, we may also expect that the influence which a substituent has on the crystal symmetry will not alone depend upon its absolute mass but may be a periodical function of the mass.

(c) *Compounds containing Several Carbon Atoms.*—When the simplest carbon radical, the methyl group —CH_3 is successively introduced into the methane molecule, taking the place of the four hydrogen atoms, we obtain ethane, propane, trimethyl-methane, and tetramethyl-methane As seen from the table on p. 2, ethane is hexagonal, propane probably rhombic, trimethyl-methane hexagonal, and tetramethyl-methane regular The crystal symmetry of these hydrocarbons corresponds thus to the symmetry of their molecules In this case the monosubstitution product and the trisubstitution product are both hexagonal (or trigonal) The molecule of ethane is peculiar in this respect, that the substituent is identical with the remaining nucleus of the compound into which it enters, and a molecule of this kind consequently possesses a higher degree of symmetry than any other monosubstitution product CH_3R.

In the case of longer carbon chains, a different degree of symmetry may in many instances be ascribed to the molecules, depending upon the view taken as to which part of the molecule may be regarded as a substituent, for example, propane may be regarded—as it is above—as dimethyl-methane, that is, as a di-substitution product, or as ethyl-methane $CH_3.C_2H_5$. In the first alternative the symmetry of the molecule would be orthorhombic, in the latter monoclinic. It seems that, in cases like this, it is correct to assume that the molecule really possesses the highest degree of symmetry which can be allotted to it. The symmetry of a long carbon chain will also largely depend upon the actual way in which the atoms in such a chain are close packed. Of the hydrocarbons containing such long chains, *n*-butane crystallises, similarly to ethane, in the hexagonal system, *n*-hexane and *n*-octane are, however, monoclinic or triclinic The experimental results with regard to *n*-pentane and *n*-heptane are less definite, but, in any case, it seems certain that the normal hydrocarbons containing more than four carbon atoms all crystallise in the systems of least symmetry It is remarkable that the two lowest members of the series containing an even number of carbon atoms should agree in their crystalline form and differ from the members containing an odd number of carbon atoms. This forms an analogy with their behaviour as regards their melting points, the lower

substituent of unsymmetrical build is introduced in the place of a symmetrically built radical, or when an atom of great atomic volume is introduced in the place of one of small atomic volume

members of the series forming two different groups, the series with an even number of carbon atoms melting, as is well known, at a comparatively higher temperature than the series with an uneven number of carbon atoms in the molecule

In tetramethyl-methane each of the four groups connected to the central carbon atom is in itself a body in space   As, however, the group —CH_3 is symmetrically built, the symmetry of the methane molecule is not diminished, but is, on the contrary, increased.   That tetramethyl-methane crystallises in the regular system may therefore be regarded as an important confirmation of the theory.   If one of the hydrogen atoms in each of the methyl groups were, however, substituted by some other atom or group, we might expect that the resulting product would not crystallise in the regular system, as the four groups in themselves would then no longer be of symmetrical build   We may therefore expect that tetra-ethyl-methane and tetra-propyl- or isopropyl-methane would not be regular, while tetra-tertiary-butyl-methane again would be regular.   These hydrocarbons have not yet been prepared synthetically   The penta-erythrite $C(CH_2OH)_4$ can, however, be regarded as tetramethyl-methane in which one hydrogen atom in each of the methyl groups has been substituted by the —OH group, thereby rendering these four groups unsymmetrical in build   As a result thereof, the molecule contains only one four-fold axis of symmetry and four planes of symmetry, instead of four three-fold axes, three two-fold axes, and six planes of symmetry.   Now, penta-erythrite crystallises in the tetragonal system, which is entirely in accordance with the existence of a four-fold axis of symmetry in its molecule   With regard to the tetra-ethyl-ether of the orthocarbonic acid $C(O\ CH_2CH_3)_4$, the case is very similar   The introduction of the ether-oxygen atom would probably not alter the symmetry of the molecule as compared with $C(CH_3)_4$, but the —CH_2CH_3 group is not of symmetrical build, and, in consequence, the molecule possesses only one four-fold axis of symmetry and four symmetry planes   In accordance therewith the ether is tetragonal, but the analogy in build of the molecule with that of tetramethyl-methane is also indicated by its pseudo-regularity.   The methyl-ether of orthocarbonic acid would probably be found to crystallise in the regular system, but this body has not yet been prepared

In the class of the alcohols, the trimethylcarbinol is of interest, as its molecule contains a three-fold axis of symmetry.   In accordance herewith it crystallises in the hexagonal system.   Of the ethers, the simplest, the dimethyl ether $CH_3.O.CH_3$, is rhombic   It is built very similarly to ethane, but on account of the introduction of the O-atom the atoms in the molecule

cannot, probably, be close packed in as symmetrical a way as in the case of ethane, the result of which is that the ether crystallises in a system of lower symmetry than ethane. If one of the hydrogen atoms is substituted by a methyl group, we obtain the methyl-ethyl-ether in which the symmetry plane passing through the O-atom of the dimethyl-ether no longer exists. This ether is monoclinic. When a hydrogen atom in the other methyl group is then substituted by a methyl group, the two groups connected with the ether-oxygen again become similar; the substitution product, the diethyl-ether, crystallises in the orthorhombic system. The influence of the degree of symmetry of the chemical molecule on the crystal form of the substance is thus distinctly shown by the ethers also.

Amongst the unsaturated hydrocarbons, ethylene is monoclinic, but acetylene regular   The atoms in acetylene will, on account of the triple linking of the carbon atoms, probably all lie in one straight line, and it is, therefore, not surprising that this body crystallises in a symmetrical way. This is also the case with other simple compounds containing a triple linking, thus K C N is regular   Acetylene-di-iodide, CI CI, as obtained from solutions at ordinary temperature, is rhombic ; this is, however, probably a modification corresponding to the double-refracting modification of acetylene which is stable at low temperature .

Ethylene occurs only in one modification, which is monoclinic, and so are also ethylene di-iodide, CHI CHI, and ethylene tetra-iodide, CI_2 CI_2, as obtained from solution at ordinary temperature   Ethylene and the tetra-iodide contain only substituents which are identical among themselves. The cause of the low degree of symmetry of the crystal form of these two bodies must therefore be sought in a deforming influence of the ethylene link Further experimental evidence is, however, desirable on this special point.

Of hydroaromatic hydrocarbons, only trimethylene, hexamethylene and methyl-hexamethylene have been investigated, as the other polymethylenes are unfortunately not easily accessible, and it would mean too great a loss of time to prepare them specially for an investigation of the present kind

In trimethylene, the three carbon atoms forming the ring must necessarily lie in one plane, and we must in consequence expect the molecule to possess one trigonal axis of symmetry and to crystallise in the trigonal system   As far as the optical investigation enables us to conclude this is also the case Hexamethylene is regular.   Of the hexa-substitution products $C_6H_6Cl_6$ and $C_6H_6Br_6$ both cis-forms and trans-forms exist.   The form of the hexachloride which is described as the " cis-form " is pseudo-regular, and the form described as the " trans-form " is monoclinic. The form of the hexachloride which is here referred to as " pseudo-regular " is one of those bodies of which it is, on

account of the optical anomalies it exhibits, extremely difficult to say to which of two crystal systems it really belongs The crystals, as measured goniometrically, are regular, but the optical properties indicate that they are hexagonal The corresponding form of the hexabromide is regular also in its optical properties. There are evidently in this case quite special circumstances —probably connected with the way the atoms in such a molecule may be close packed—which render it possible for the molecules to assume a higher degree of crystalline symmetry than the hexagonal which would correspond to the actual degree of symmetry of the molecule if we assume that the six carbon atoms all lie in one plane If one of the hydrogen atoms in such a molecule of hexagonal symmetry is substituted the symmetry is changed to monoclinic An example thereof is furnished by monomethylhexamethylene, which actually is monoclinic

We then pass over to the aromatic compounds. Benzene itself is orthorhombic. Toluene is also orthorhombic, and thus substitution of a hydrogen atom by a methyl group does not affect the crystal system A di-substitution in the para-position, however, distorts the orthorhombic symmetry of the benzene nucleus para-xylene is monoclinic If several methyl groups enter into a symmetrical position in the benzene molecule, the crystal symmetry is not changed ; mesitylene and hexamethyl-benzene are orthorhombic

From the composition C_6H_6, one might expect that benzene itself should be hexagonal It is, therefore, probable that the double links, or whatever may be the peculiar disposition of the valency forces in the benzene nucleus, here, as in the case of the ethylene derivatives, are instrumental in bringing about a lower degree of symmetry of the molecule than that which it might be expected to have As the build of the benzene nucleus itself is not altered by substitution of the hydrogen atoms, and as the phenyl group, moreover, is a group of comparatively large mass, those circumstances which affect the symmetry of benzene itself will also manifest themselves in their effect upon the symmetry of the compounds into which phenyl enters as a substituent If we thus consider the successive substitution products of methane in which the phenyl group is the substituent, we have toluene, $CH_3.C_6H_5$, diphenylmethane, $CH_2(C_6H_5)_2$, triphenylmethane, $CH(C_6H_5)_3$, and tetraphenylmethane, $C(C_6H_5)_4$, which are all orthorhombic In all these cases the nucleus of the parent substance is very small in comparison with the phenyl group or groups, and it is therefore of very little morphotropic influence on the symmetry of the phenyl groups, which remains dominant.

Isomorphism, Morphotropy, and Enantiomorphism from the Point of View of the Theory

In the introduction to Part I of this paper[*] it was pointed out that the phenomena of isomorphism, of morphotropy, and of enantiomorphism each indicated the existence of a general relationship between the crystalline properties of a substance and its chemical constitution, although sufficient data were not previously known which might have served to establish a theory, correlating and explaining the evidence as established separately by these phenomena   If the theoretical views on the interdependence of the chemical constitution and crystal form of the simpler organic bodies arrived at in the preceding chapters are correct, they must not only enable us to give an explanation of the isomorphism of complicated bodies and of the phenomena of morphotropy and of enantiomorphism, but also of the mutual relationship between these three phenomena.

If we compare two isomorphic bodies with one another, we find that their molecules differ only in this respect, that an atom of a certain element in one is in the other replaced by an atom of a chemically related element   The general architecture of the molecule and its symmetry are not affected by such a substitution   If, however, instead of an atom of the same valency and of similar properties an atom of a different valency and of different nature altogether is introduced, then the atomic spheres of influence of the other atoms in the molecule will be sufficiently affected to cause changes of a more general kind in the symmetry conditions of the molecule, and the product will, in consequence, no longer be found to be isomorphic with the parent substance   *The phenomena of isomorphism are thus explained by the fact that elements which are able to replace each other isomorphically are sufficiently similar to cause no alteration of the symmetry of the molecule when replacing each other.*   The atoms replacing each other isomorphically have, however, a different atomic volume, and we must therefore expect that the amount of space they occupy will manifest itself in the crystal dimension of the bodies   Now this is exactly what happens in isomorphic series   The exact measurements by Tutton have shown that the change in crystalline dimensions of isomorphic bodies may, even to their numerical value, be deduced from the space occupied by the atoms which replace each other isomorphically.

In an entirely analogous way the phenomena of morphotropy are explained by the theory of the interdependence of crystal symmetry and molecular symmetry.   If an atom or radical in a comparatively large molecule is

* 'Roy. Soc. Proc.,' A, vol. 88, p 354 (1913).

replaced by another atom or radical, a more or less strong deformation of the atomic spheres of influence takes place according as the new substituent is more or less similar to the original one. The substitution will manifest itself in a gradual change of the crystal form to a form more and more different from that of the original parent substance, as the substituent becomes more and more different in character or degree of symmetry from the original substituent, or as the mass of the substance becomes larger in comparison with that of the nucleus into which it enters.

These circumstances afford also the explanation of the fact that some bodies of a rather complicated constitution crystallise in the regular crystal system, they contain a comparatively large number of atoms and radicals distributed in a way which makes the molecule sufficiently symmetrical to cause it to crystallise in the regular crystal system, and the unsymmetrical groupings of atoms which may be contained in such a molecule are not of sufficient "morphotropic influence" to cause an alteration of the general symmetry of the molecule as manifested in its crystal form.

Lastly, with regard to the enantiomorphism, Pasteur was the first to prove that substances which in the liquid or dissolved state are able to rotate the plane of polarisation crystallise in enantiomorphic forms. Becke then showed that, independently of the crystal system in which a substance of this kind crystallises, such enantiomorphic forms always belong to one of those nine crystal classes which contain neither planes of symmetry nor planes of compound symmetry but only axes of symmetry.[*] Becke also pointed out that a chemical molecule which contains an "asymmetric carbon atom" in the sense of van't Hoff and Le Bel is devoid both of planes of symmetry and of planes of compound symmetry. The enantiomorphism of optically active substances is therefore a further consequence of the general law of the interdependence of the crystal symmetry and the molecular symmetry. In this case it is the lack of symmetry of the molecule, which is reproduced in the crystals by a corresponding lack of planes of symmetry. The law of Pasteur, therefore, from this point of view appears as a special case of a general law.

As the law of Pasteur holds good also with regard to molecules of very complicated build, of which it is not possible at present to say definitely what mutual arrangement the atoms occupy inside the molecule, we are justified in concluding that the general law of the interdependence of molecular symmetry and of crystal symmetry applies even to such complicated cases. As an example in which this is actually proved by investigation, the group of the

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* F Becke, 'Tschermak's Mineralog. und Petrogr Mitteil,' vol. 10, p. 464, and vol. 12, p 256.

alums, $(SO_4)_4Al_2K_2.24H_2O$ (in which $K = Na$, Li, Rb, Cs, NH_4, $Al =$ Cr, Fe), may be quoted. The alums containing the alkaline metals and aluminium or chromium all crystallise in the "dyakis-dodecahedral" class of the regular crystal system. It is probably the disposition of the 24 H_2O groups which gives the molecule a sufficient degree of symmetry to crystallise in the regular system, and the mutual arrangement of the atoms in the group $Al_2K_2(SO_4)_4$ does not interfere therewith. Crystals belonging to the dyakis-dodecahedral class of the regular system are characterised by three two-fold and four three-fold axes of symmetry and by three planes of symmetry at right angles to the three two-fold axes. Ammonium alum crystallises similarly to the alkaline alums, and so does also trimethylamine alum. The active amylamine alum, however, crystallises in the "tetrahedral-pentagonal-dodecahedral" class, which is characterised by the same number of axes of symmetry, but in which no planes of symmetry occur. By the introduction into the molecule, in the place of the symmetrical CH_3 group, of the active amyl group, the general regular character of the alum molecule is thus not altered, but as the molecule can now no longer contain any planes of symmetry, this particular alum, as a consequence, crystallises in a class of the regular system devoid of symmetry planes.

The general results to which this investigation has led thus enable us to explain the phenomena of isomorphism, as well as of morphotropy and of enantiomorphism, as all depending on one and the same fundamental relationship governing the interdependence between the molecular constitution and the crystal form of a body, and which may be summarised thus "The symmetry of the chemical molecule of a substance determines its crystal symmetry."

General Considerations as to the Qualitative and Quantitative Side of the Theory

The relationship between the molecular constitution and the crystal symmetry has been discussed here from the general, that is to say, qualitative, point of view and the solution of the problem arrived at is also of a qualitative kind. No common quantitative, numerical solution of this problem of course exists, but the influence of each radical or atom upon the numerical crystallographical data has to be studied separately in each case, not only from the point of view of the effect produced by the substituent on the nucleus into which it enters, but also with regard to the effect the nucleus produces on the substituent. Investigations on isomorphic and morphotropic series furnish the numerical data in each special case.

The mutual relation between the qualitative and quantitative inter-dependence of molecular constitution and crystal-form is, in a way, similar to what is the case regarding the optical rotatory power of organic com-pounds. The theory of the "asymmetric carbon atom" solved this problem quite generally in a qualitative sense, but the determination of the actual numerical influence of each atom, or group, on the total rotation of the compound meets with great difficulties

Extension of the Theory to Compounds other than Carbon Compounds

The existing data concerning other tetravalent elements indicate that the theory developed here for the interdependence of molecular and crystal symmetry of the simpler organic compounds may be extended to other compounds, in a similar way as the theory of the asymmetric carbon atom Thus the following compounds of the general type AR_4 are regular SiI_4, TiI_4, SnI_4, $IrCl_4$, UCl_4, and the following compounds of the type AX_2R_2 are orthorhombic $Sn(CH_3)_2Cl_2$, $Sn(C_2H_5)_2Cl_2$, $Sn(C_3H_7)_2Cl_2$, $Sn(CH_3)_2(CHO_2)_2$. No data are available at present concerning compounds of the types AXR_3 and AX_3R. Further investigations are therefore necessary, and the author intends to extend this research to Si, Ti, Sn, Pb, and other compounds However, the cases mentioned above make it already now almost certain that the relation expressed by the theory is not limited to carbon compounds.

The Relationship between the Chemical Constitution and the Occurrence of Polymorphic Modifications

With regard to the relationship between the chemical constitution and the occurrence of polymorphic modifications, the following may be said already at this stage of the investigation Vorlander has shown, as a result of his elaborate investigations on the occurrence among organic bodies of liquo-crystalline modifications, that the existence of such modifications is intimately connected with the occurrence of long carbon chains, and with the occurrence of para-substituents in the benzene nucleus. As the liquo-crystalline modifications must be regarded as a kind of polymorphic modifications, it seems not improbable that the occurrence of polymorphism is actually a constitutive property The existence of polymorphic modifica-tions of nearly all the simplest substitution products of methane confirms this view It further suggests that methane itself also might be poly-morphic Methane was therefore investigated at liquid hydrogen temperatures, and it was found that an enantiotropic transition into a double-refracting modification really takes place at a very low temperature, quite analogously to what is the case with respect to the other carbon compounds of the type

CR₄.—It has, further, been noticed that the position of the transition point in the substitution products of methane relative to their melting point is influenced in a regular manner by the nature of the substituent The transition points situated at low temperature have, however, so far been determined only quite approximately, and a more detailed discussion of this question must, therefore, be postponed until more accurate temperature determinations have been made

Before concluding this paper, I have to acknowledge the liberality with which the technical resources of the Davy-Faraday Laboratory, in which the investigation was carried out during the year 1912 and the earlier part of 1913, have been placed at my disposal I wish also to thank Sir James Dewar for the interest he has shown in this work, whereby he has greatly furthered its progress.

On a Meteoric Iron from Winburg, Orange Free State.

By W. A. DOUGLAS RUDGE, M.A.

(PLATES 1 AND 2)

Some account of this meteorite has been given in the 'Transactions of the Royal Society of South Africa,' 1912, vol 2. The present communication deals more fully with the internal structure of the meteorite, giving also some account of the mechanical and magnetic properties

The meteorite was seen to fall in 1881 by some natives working on the Zeekoegat farm, belonging to Dr. Schneehage. They reported the matter to their employer, who ordered them to carry the meteorite to the farmyard, where it remained some years, finally being sent to the Bloemfontein Museum. The meteorite measured 38 by 23 cm. along the two greatest axes and weighed nearly 50 kgrm. It was slightly magnetic, having a number of poles. It will be convenient to divide this paper into sections, viz —

(1) Dealing with the chemical composition.
(2) „ „ internal structure.
(3) „ „ mechanical properties.
(4) „ „ magnetic properties

c 2

1 *Chemical Composition.*

The meteorite is not very uniform in composition, owing to the veins of alloy which run through the mass, and a qualitative examination showed that it consisted mainly of iron and nickel, with some pulverulent carbon, which separated when the material was treated with dilute sulphuric acid   Traces of phosphorus and silicon were also present   On solution of the metal in dilute acid the gas evolved was almost odourless, so that it seems unlikely that the carbon was combined   The nickel does not appear to be uniformly distributed throughout the mass of the meteorite, as it is possible to separate from the mass flakes of an alloy of iron and nickel, in which the proportion of nickel is far greater than that for the whole meteorite. The iron is probably present in two forms (1) as large ferrite crystals, and (2) in the iron-nickel alloy   That present in (1) dissolves readily in dilute sulphuric acid, whilst (2) requires strong hydrochloric acid to make it go into solution along with the nickel   If a small lump of the metal is very slowly dissolved by sulphuric acid of about normal strength, flakes of the alloy, sometimes more than 1 cm in length and mostly triangular in shape, remain behind.   These flakes are strongly magnetic and retain their susceptibility up to a red heat   The quantitative analysis was directed to obtain information on the following points ·—

(1)   The iron soluble in dilute sulphuric acid
(2)   Total iron.
(3)   Total nickel.
(4)   Nickel contained in the flakes of alloy insoluble in dilute
            sulphuric acid.

(1) This was ascertained by treating a weighed portion of the metal with dilute sulphuric acid, in a flask closed by a Bunsen valve, until all action had ceased, and then titrating the solution with decinormal bichromate in the usual manner   The mean of twelve determinations gave 90 67 per cent for the iron soluble in dilute acid

(2) A weighed portion of the metal was heated for some time with strong hydrochloric acid to which a very small crystal of potassium chlorate was added, and the flask closed with a Bunsen valve, and after reduction with magnesium the solution was titrated with decinormal bichromate   The mean of six determinations gave 92·54 per cent for the total iron.

(3) The nickel was at first determined by Moore's method as described in Crookes's 'Select Methods,' p. 225, but consistent results were not obtained, and the method attributed to Jamieson, and described in Sutton's 'Volumetric

Analysis' at p 269, was used instead. Control experiments with solutions containing known amounts of nickel and iron gave confidence in the method.

The mean of six determinations gave 6·905 per cent for the nickel

The composition of the metal appears to be :—

Iron soluble in dilute sulphuric acid . .	90 67
Iron insoluble in dilute sulphuric acid .	1 87
Nickel	6 905
Carbon and undetermined ..	0 555
	100 000

(4) The metal as a whole is not very homogeneous, as the veins of alloy and the flakes also vary considerably in thickness About 20 to 30 grm of the turnings from the meteorite were digested in normal sulphuric acid for three days. A residue, which consisted of about 2 5 per cent of a mixture of finely granular carbon and shreds of alloy, remained behind The alloy was separated from the carbon by means of a magnet, and after solution in nitric acid the nickel was estimated by the method already referred to The mean of two analyses gave 29 57

The carbon has not been actually determined, but by mechanical means aided by a magnet the amount of carbon separated from the residue insoluble in dilute sulphuric acid was not more than corresponding to 0 15 per cent of the meteorite A portion of the residue was very insoluble and resisted prolonged treatment with aqua regia. It consisted of some glistening fine grains which were decidedly magnetic, the actual quantity was, however, small and escapes observation unless a large amount of the meteorite is used

I believe that the nickel is contained in the alloy, which is disseminated throughout the mass in three distinct forms —

(a) As large veins running through the mass.

(b) As plates separating the large crystals of ferrite.

(c) As small crystallites, embedded in the ferrite itself, and as small grains.

The small crystallites cannot be isolated, and on solution of the ferrite remain behind as fine silvery threads The pitting seen when a slab of the meteorite is exposed for a long time to the action of dilute acids points to a local galvanic action taking place around embedded grains of alloy. It is possible that the different portions, a, b, c, may have different chemical compositions.

2. *Internal Structure*

The meteorite was cut across.   The metal is quite soft and may easily be cut by a knife, and is very malleable, with harder patches occurring here and there.   After cutting, both surfaces were polished in the usual way, one being left bright and the other etched   In the former the larger veins of alloy running through the mass may readily be seen, and the latter, after etching with dilute nitric acid, showed the ordinary "Widmannstatten" figures so characteristic of meteoric iron, but, on submitting the section to a magnification of about 12 5 diameters, the large crystals of ferrite are seen to be separated from each other by well defined boundaries composed of some other material, which in some cases penetrates into the ferrite masses These effects are best seen under slightly oblique illumination and cannot be done justice to by photography   Fig 1 (Plate 1), is a magnified portion of the surface   Patches of the alloy can be seen, and a number of small apparent projections are clearly indicated   These seem to be small isolated portions of an alloy which stand out owing to their high reflecting power, and which one would imagine had a different composition from that separating the large ferrite masses

There is a considerable difference in the solubility of the ferrite, as compared with that of the alloy, as is shown by fig 2   This was obtained by covering over a small block of the metal with wax, with the exception of one face, the block being supported in dilute sulphuric acid so that the face could be attacked.   The ferrite was eaten away by the acid, but the alloy was not attacked and the bright lines indicate the flakes of alloy separating the large crystals of ferrite.   The rough pitting on the attacked surface is, I think, caused by the presence of small specks of the alloy such as are seen in fig 1 The most satisfactory method of examination of the finer structure is by heat-tinting, rather than by etching, as then the beautiful structures of the crystals of the alloy are clearly seen, but all efforts to obtain satisfactory photographs have failed, even with the use of isochromatic plates.   Figs. 3 and 4 are photographs of a small section after etching with dilute nitric acid. The remarkable shapes of the crystallites are here clearly shown, and also the remarkable parallel orientation they show with reference to each other. These fine crystallites are very delicate and fragile, and on dissolving a piece of the metal in dilute sulphuric acid they break up into fine silvery threads. In the heat-tinted specimen the lines are a deep gold upon a blue ground.   In fig. 4 attention is called to the fine parallel lines shown on the large etched ferrite grains and, by appropriate illuminations, another set of lines is seen crossing these at right angles.   Heating had an important influence in

Fig 1

Fig. 2.

Fig. 3.

FIG. 4.
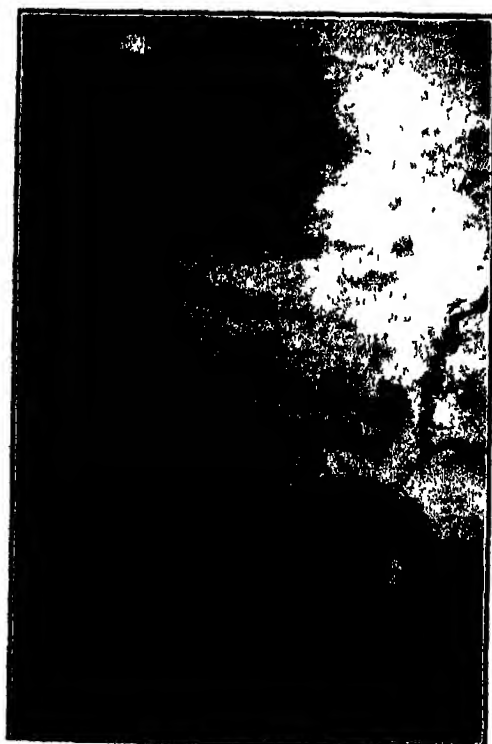
FIG. 5.

FIG. 6.

modifying the structure of the iron.   Fig 5 is a photograph of the same specimen under a magnification of six after heating to about 800° C for half an hour, and then allowing to cool slowly   After cooling, it was polished and treated with the same etching agent, when it appears that the structure has been more or less broken down   Lines of the alloy can still be readily traced, but the well defined outline of the ferrite crystals has disappeared   The temperatures were determined by the Fery pyrometer.

The meteorite may be considered as being formed of a mass of ferrite crystals, with plates of alloy separating the crystals, and with eutectoid crystallites disseminated throughout the ferrite, and with veins of alloy running in definite directions   The crystallites themselves are composed of a number of thin laminae, arranged according to some definite plan

3 *Mechanical Tests*

The coarse-grained structure of the metal made it appear to be of interest to submit it to some mechanical tests, and, with this object, a piece of metal, measuring about 5 inches in length and nearly $\frac{3}{4}$ inch square, was cut out of a portion which seemed to be free from the large veins   This had threads cut for a distance of $\frac{3}{4}$ inch on each end, and the remaining portions were machined up to $\frac{1}{2}$ inch square, the surfaces being polished and etched   It was then seen that several veins ran across nearly to the centre of the specimen, and, in order to get the sample as homogeneous as possible, a portion was planed away, so that the final section was triangular when the veins had been cut away   The specimen was mounted in the large testing machine in such a way as to allow of examination by a microscope, or to permit of the application of the extensometer   A load was applied gradually, and the form of the crystal grains watched and photographed under a magnification of about 100 diameters, in order to detect any change occurring in the etched pattern on the surface, but, within the limits of the strength of the material, no definite change could be seen   Photographs were taken under dead loads of 0 5, 1, and 1 8 ton, without any difference being observed in the form of the boundaries   The break took place very sharply under a load of 10 25 tons per square inch

The fracture (fig 6) shows clearly the large-grained crystalline structure of the material   At first sight it would appear as though the comparatively large plane surfaces shown on breaking, the edges of which are clearly shown in the photograph, were cleavage planes developed in the crystal The broken surfaces were, however, not bright, as would be the case with an ordinary sample of steel or iron, but were pitted to some extent on one

surface, whilst small specks of bright nickel-iron alloy occupied corresponding positions on the other surface, that is, there was clearly a lack of continuity at the surfaces   Some of the thin alloy plates separating the crystals could also be seen   It was not easy to obtain an end-on view of the fracture, but the side view shows clearly that the fracture took place along the junction of crystal planes. The break does not in any way resemble a flaw, but is just what one sees in the breaking up of any highly crystalline material, such as sugar candy   From the extension, before the break, the value of Young's modulus may be found   Taking the extension between 0·5 and 1 5 tons on either the loading or unloading curves as lying within the elastic limit of the material, we get a value for Young's modulus of 3×10^7 lbs per square inch

Compression Test —A piece of the metal in the form of a parallelepiped was prepared, having a size of $1 8 \times 0 7 \times 0 87$ cm , and carefully polished until all the coarse scratches had been removed   This was then placed between two steel cylinders and compression gradually applied, the specimen being watched through a microscope.   Very little change was noted until the dead load reached a value of 4000 lb, when the mass seemed to be cleaving into a number of separate large-sized crystals, and, on increasing the load to 6000 lb, this became very marked   "Slip bands" now made their appearance, but were not very well defined until a load of 7000 lb had been applied, when they were clearly visible, but difficult to photograph, because the originally plane surface was now very much corrugated.   The shape of the end section was much changed, appearing as though a twisting stress had been applied.

4 *Magnetic Tests*

The magnetic properties of the metal were tested by Ewing's permeameter for fields of moderate strength   A rod of the metal 4 2 inches by 0 25 inch was turned up on the lathe   The portion selected was one free from large veins, but it showed on etching the usual large-grained structure. This was placed in one of the coils of the permeameter, a standard bar being placed in the other   The B and H curves from the two bars are shown in Curve 1, where it is seen that for weak fields the permeability is greater than that of the standard Swedish iron but with strong fields it becomes slightly less.

For strong magnetic fields, the apparatus as used by Prof. Hopkinson, and described in 'Proc. Inst Elec Engineers,' vol. 46, was employed.   In the arrangement, two small pieces of metal as nearly identical as possible were taken, one being the standard, and the other the specimen under
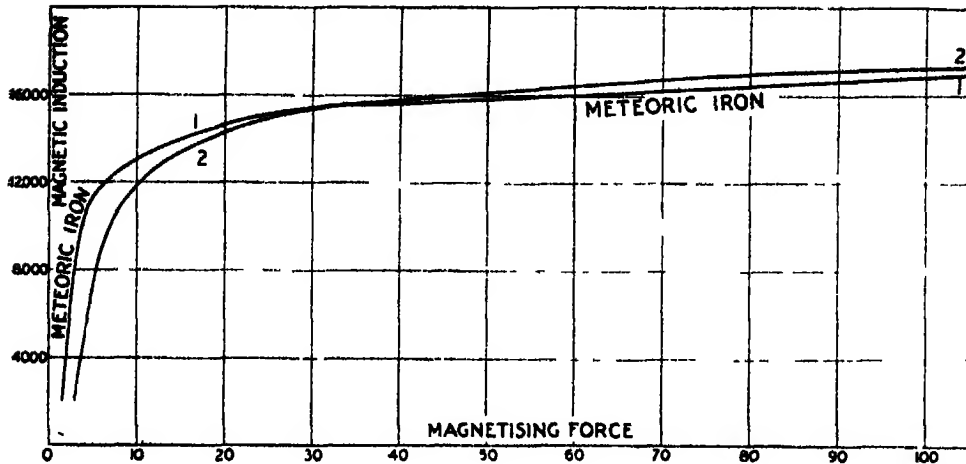
examination. The induction through these was compared for the same value of the magnetising force As a mean of many measurements made on six specimens the susceptibility of the meteoric iron as compared with that of the Swedish standard was as

1670   1680

By annealing carefully the susceptibility was increased

My thanks are due to Prof Hopkinson for kindly permitting me to make use of the Engineering Laboratory in Cambridge, and also for the kindly interest he took in the work—and also to his assistant, Mr H Quinney, for the very great assistance he gave me in carrying out the various tests, and finally to the Committee of the Bloemfontein Museum for placing the meteorite at my disposal

Summary.

(1) The meteorite is composed of a mass of ferrite crystals, with veins of iron-nickel alloy running through, and with flakes and crystals of iron-nickel alloy disseminated throughout the mass

(2) The mechanical strength of the metal is not so great as that of ordinary iron, but before rupture occurs the modulus of elasticity is nearly as great as that of ordinary iron

(3) The individual crystals are soft and malleable,

(4) On applying a crushing force, the iron tends to cleave into definite crystals.

(5) The magnetic properties are practically the same as those of Swedish iron.

Chemical Action that is Stimulated by Alternating Currents.

By S G BROWN

The following experiments were carried out in the year 1905   Taking a simple voltaic cell, consisting of an anode and cathode of zinc and carbon, and an electrolyte of dilute sulphuric acid, it was found that polarisation, which takes place when the cell is joined to a local circuit of low resistance, could be diminished or completely abolished, by passing through the cell an alternating current of suitable value.   Fig 1 illustrates the arrangement of the cell, D, joined up to deliver current through the ampèremeter, B , under
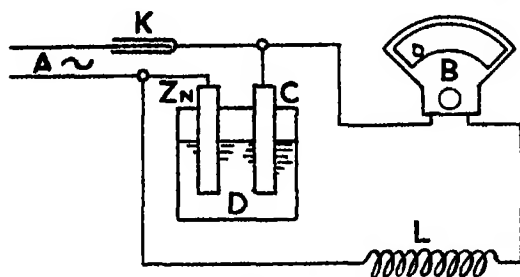
Fig 1

these conditions the cell is very quickly polarised, and the continuous current falls to a very low figure

On the other hand, if a suitable strength of alternating current of, say, 100 periods per second is sent through the cell from the leads A, the cell D will be completely depolarised and will give its full current delivery.   L is a self-induction and K a capacity to prevent the alternating and continuous currents from flowing in each other's circuit, the only part of the circuit common to both being through the cell

If the alternating current has a frequency of, say, 12,000 periods per second, and we place a carbon transmitter in its circuit, on speaking into the transmitter the speech will be very correctly reproduced, by variations correspondingly produced in the value of the continuous current from D, and the voice will be heard correctly in a telephone included in the circuit with B   This shows that the rise and fall in the value of the continuous current immediately follows that of the mean strength of the alternating current.

The polarising effect in the cell is caused, as is well known, by the coating

of gas bubbles on the cathode, when the alternating current is switched on not only is the production of gas increased, due to the increased output of current from the cell, but the gas bubbles appear to shoot away at right angles to the surface of the cathode

Another arrangement of the cell, as shown in fig 2, was tested under similar electrical conditions, and in this case the cathode had a large surface exposed, and the zinc anode was just touching the liquid so as to only expose a small surface to the action of the electrolyte   Under these conditions, and keeping the cell free from vibration, something similar to polarisation sets in and the current delivery, which is at first large, soon falls to a very low value   The action of this cell was the same if the carbon was exposed to the electrolyte directly or placed within a porous cell in contact with strong nitric acid, proving that the falling off of current was not due to gaseous polarisation but to the restrained chemical action on the zinc anode caused by the depletion of the active properties of the electrolyte in immediate contact with the anode.   The effect of the alternating current was the same as before, and the cell under the stimulating action would greatly increase its current delivery, proving that in some manner the alternating current increases the solvent action of the electrolyte on the anode

I have indicated diagrammatically the final state of the cell in fig 2, before the alternating current is applied   A shows the depleted area around the
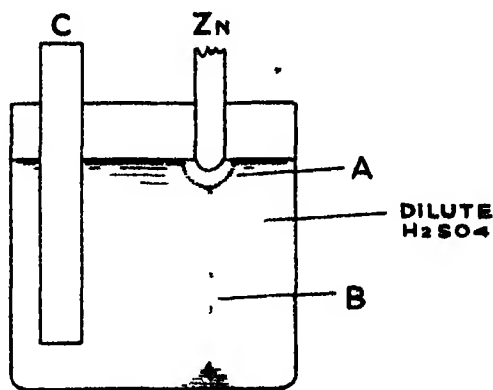
Fig 2.

zinc anode, the sulphuric acid ions have to be projected or diffused through this area before they can unite with the zinc to form zinc sulphate   This sulphate, although colourless, can be observed, by the refracting action on light, to be falling in a thin steady stream B to the bottom of the cell. The alternating current appears to increase the velocity of the ions in some manner and enable them to traverse the depleted area and dissolve

more zinc   This is seen by the increase in the zinc sulphate stream and the larger current supplied by the cell

By making the surface of the anode in contact with the electrolyte small in area, the action of the alternating current will be concentrated and the ions will be correspondingly increased in chemical activity   In one case the anode was constructed of a fine platinum wire dipping about one-tenth of an inch into the dilute sulphuric acid and an external battery of two volts applied   When the alternating current was superimposed the platinum started to oxidise, and in a short time the whole of the wire in contact with the liquid was turned into a black powder   The same thing happened with gold, the wire turned into a yellow insoluble powder   With the filament of a carbon lamp as anode the carbon was completely dissolved or turned into gas ; and, in fact, no conducting material could be found that would resist the combined action of the two currents when applied in this concentrated manner

These experiments were carried out with alternating currents at a frequency of 12,000 periods per second, as it was thought that the stimulating effects were much greater at high frequencies, but no tests were made to prove this point

Many forms of cells and batteries were tried, and it was found that in every case where the anode was constructed of a soluble metal, and was arranged to project as little as possible into the electrolyte, the alternating current would stimulate the chemical action and force the cell, or cells, to deliver a greater output of current   Also, several metals that were insoluble in the liquid without the alternating current became soluble when this current was applied

Another action of alternating currents was illustrated by the following experiment   In fig 3, the circuit of the 2-volt battery was interrupted by the
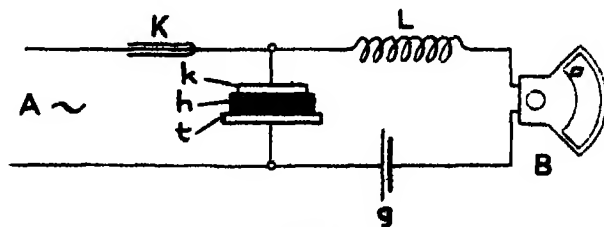
FIG 3

cake of compressed oxide of lead placed between the bright lead plate, *k*, and a platinum anode, *t*. The current flowed from the platinum to the lead so as to make the lead plate the cathode.   In this direction the cathode did not

oxidise, and a maximum current passed through the arrangement. When a high-frequency current was applied an increase in chemical action took place, which oxidised the lead plate superficially and produced a back E.M.F, and thus reduced the continuous current through the cell Here we have a case of stimulated chemical action without the use of a fluid dielectric Other metals were tried in place of the lead, and in every case it was found that the continuous current fell when the alternating was applied, but only three metals were found that would allow the continuous current to spring back to its original high value as soon as the alternating currents were discontinued These three metals were bismuth, lead, and thallium, and they required 3, 2, and $1\frac{1}{2}$ volts in their local batteries respectively to give the best results The function of the alternating current is to stimulate the chemical changes, it may be to produce oxidation as in the foregoing experiments, or in other cases it may be to reduce the oxide, although no direct test was made to prove this supposition

I think that these experiments explain the action of the Branley filings coherer—a device in which the group of granules act normally as an insulator, but become conductive when high-frequency currents such as Hertz waves pass through them Iron or nickel filings are insulated from each other by a thin film of oxide, but the coherer has a small capacity, with the oxide as dielectric, and the waves are thus allowed to pass The rapid alternating currents act upon the oxide dielectric and, by stimulating chemical action, reduce the oxide at the points of contact to a metallic or conducting form and allow a continuous current to flow When the tube is shaken the oxide again intervenes and another application of the alternating current is required to produce conduction

The actions that I have here indicated seem to me to be much like that which takes place in many catalytic processes a chemical action taking place between two substances only when a third substance is present, although the third substance does not seem to suffer any chemical change itself It may be possible, therefore, that the combined action of the alternating and continuous currents will be of value in electro-chemical processes

It was at one time hoped that by applying a small alternating current to a cell it would be possible to unlock a much greater continuous current in return, or in other words that the cell would act as a relay, but from many tests it would seem that this cannot take place, and in no case was the continuous current output of energy greater or as great as the ingoing alternating energy of the stimulated cell.

Fig. 4 shows the connections as arranged to test numerically the effects of the high frequency currents in the cell or cells, D. The high frequency was
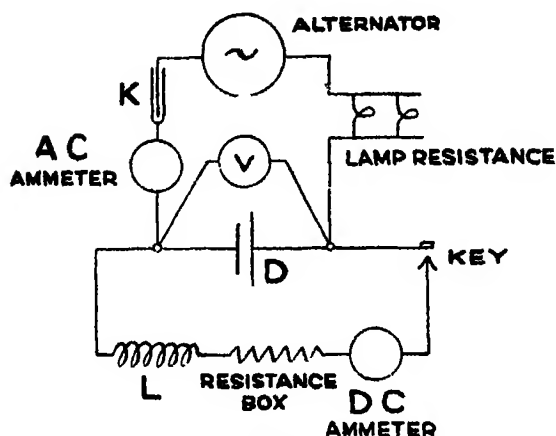
Fig 4

run throughout to give 12,000 oscillations per second   The other essential features of the arrangement are —

K,   a capacity of 1 microfarad

AC, a twisted strip ampèremeter with shunts.

DC, a moving coil milliampèremeter

V,   an electrostatic voltmeter charged inductively

L,   a large magnetic shunt of about 10 henries and 15 ohms resistance.

The alternating current was controlled by incandescent lamps and the continuous current by a resistance box

The battery of cells, D, had a zinc-carbon element with an unamalgamated zinc rod 5/16 inch diameter with a pointed tip   The carbon rod had a diameter of 3/8 inch, 2 inches being exposed to the liquid, which was dilute sulphuric acid of sp gr 1 200.

The results of the experiments are given in figs. 5 and 6

Curve 1, fig 5, represents the relation between the alternating and continuous current when the zinc just touched the liquid   Ten cells in series were used, and the continuous current was short-circuited through the milliampèremeter

Curve 2 represents the results with the same arrangement, except that a resistance of 150 ohms was inserted in the milliampèremeter circuit

Curve 3 refers to the case where two sets of five cells in parallel were connected in series.   The zero of the vertical scale is here displaced as indicated by the outer figures

Experiments were also made with a single cell   The results are given in fig 6, the different curves refer to differences in the arrangement as follows ·—
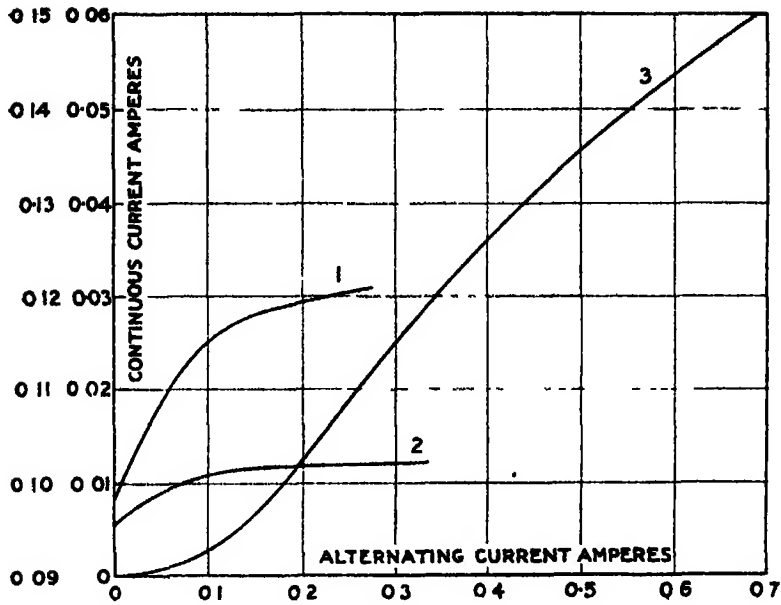
Fig 5
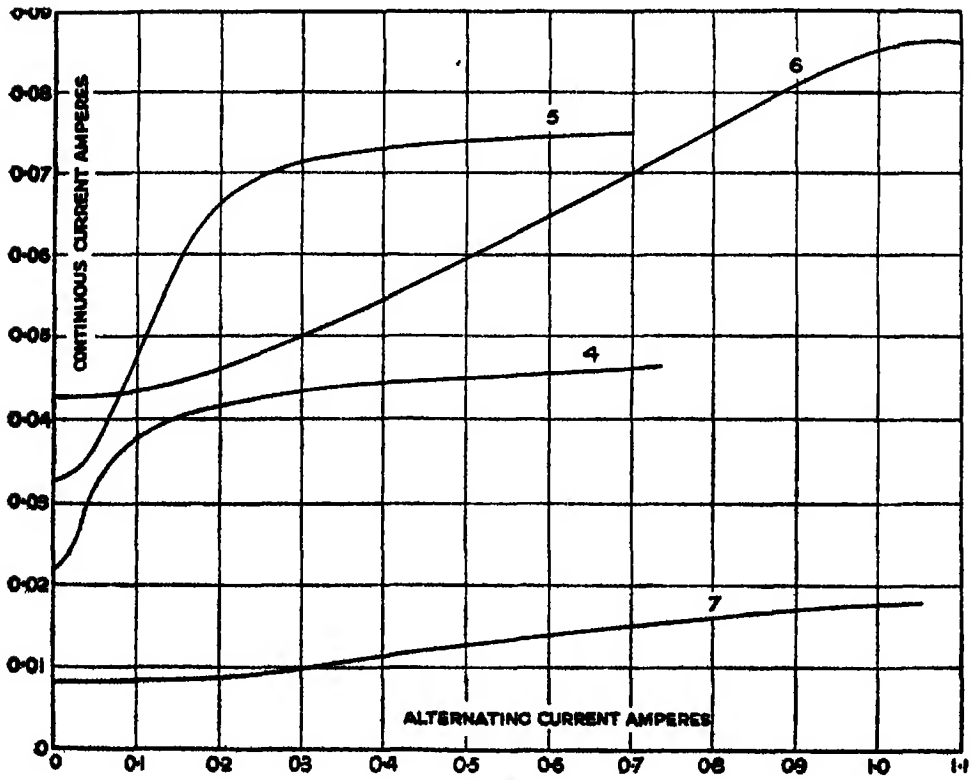
Fig 6

Curve 4   The current passed through one cell in which 2 inches of carbon was exposed, but only the tip of the zinc rod touched the liquid   The values given for the continuous current are for short circuit through the ampère-meter in this and the following

Curve 5   2 inches of carbon rod and ¼ inch of zinc rod exposed

Curve 6   2 inches of carbon rod and 2 inches of zinc rod exposed

Curve 7   Carbon tip only and 2 inches of zinc rod exposed

The results may be summarised as follows —

(1) The effect of a given alternating current was much larger when all the cells were in series than when two sets, of five cells each, in parallel were used   The ratio of the increase was approximately, with the cells in series, change in alternating current   change in continuous current   5   1 with 10 cells in series

With two sets of five parallel cells, change in alternating current   change in continuous current · 12   1.

(2) While the surface of the carbon exposed to the electrolyte only affects the results in so far as it increases the resistance of the cell, the current density at the zinc electrode alters the change in the continuous current greatly.

On the Effect of the Gangetic Alluvium on the Plumb-line in Northern India.

By R D Oldham, F R S

For some years past, the Annual Reports of the Survey of India, and of the Indian Government Board of Scientific Advice, have contained references to the remarkable character of the deflections of the plumb-line at stations near the southern edge of the Himalayas.   These facts, and the explanation which has been adopted by Colonel S G Burrard, Surveyor-General for India, have recently been brought into prominence by the publication of a memoir* on "The Origin of the Himalayas," certain parts of which are in contradiction with the conclusions, regarding the structure of the range, that had been drawn from geological observations

Briefly stated, the geodetic facts are as follows.   Along the southern edge of the Himalayas very high northerly deflections, amounting to about 40″ of

* 'Survey of India,' Professional Paper No. 12, Calcutta, 1912

arc, are found, which rapidly decrease in a southerly direction by about 30″ in as many miles, after which the decrease becomes much more gradual, and ultimately, a southerly deflection comes in   In a northerly direction, also, there is a decrease of deflection, though not so rapid as to the south, and stations up to 30 miles from the edge of the hills, in spite of being nearer to the main range, show a decreasing northerly deflection, which may be as much as 20″ less than that of the marginal stations.*

These peculiarities become even more marked if, instead of the observed deflections, attention is turned to the residuals, or differences between the observed deflections and those which are deduced by calculation as the effect of the visible topography   This has been done for a number of stations in India by Major H L Crosthwait,† using Mr Hayford's method of allowing for the compensation due to isostasy   With regard to this method, it may be remarked that, whether the hypothesis of isostasy adopted by Mr Hayford is correct or not, his method of calculating the effect of compensation appears to give results which are not far from the average effect, and therefore the departure of the observed from the calculated deflections, at any individual station, may be regarded as the effect of a local departure from average conditions

Regarded in this light, the residuals, which have been calculated as deflections in the meridian, may be converted into deflections normal to the general course of the range, which does not run due east and west at any of the stations dealt with by Major Crosthwait   This procedure is further justified by the figures given for Dehra Dun, at which the deflections and residuals were calculated both in the meridian and in the prime vertical, and at which the resultant of the residuals is normal to the general course of the range.   I have therefore converted the figures given by Major Crosthwait into deflections normal to the range, and measured the direct distances from the main boundary of the Himalayas.

Confining attention to those stations which lie within 50 miles to the south and 20 miles to the north, being the tract within which, as will be shown further on, the effect of the alluvial filling of the Gangetic depression could be expected to be conspicuous and predominant, data are available for ten stations in all, but four of these cannot be taken into consideration One, Murree, because the Himalayas are separated from the Gangetic alluvium by the intervening plateau of the Potwar and the Salt Range, two,

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* For details, see 'Phil. Trans.,' A, vol. 205, pp 289–318 (1905) , the original account is contained in 'Operations of the Great Trigonometrical Survey of India,' vols 11 and 18.

† 'Survey of India,' Professional Paper No. 13, Calcutta, 1912.

Pathardı and Sora, because the distance from the main Himalayan boundary cannot be determined, as it lies in Nepal, and a fourth, Birond, because it is an isolated station, with no other near enough for comparison   On the other hand, we may safely add another station, Rajpur, which is very important, as it lies close to the main Himalayan boundary   No separate calculation has been made of the effect of the visible topography, but, as it lies about half-way between Mussooree and Dehra Dun, which are about 10 miles apart, the effect of all but purely local topography will be the same as at those stations.   From an examination of the maps available, I estimate the effect of this local topography to be equivalent to a northerly deflection of about 6″ greater than at Mussooree or Dehra Dun,* and, the observed deflection being 10″ greater, the residual in the meridian becomes −17″, or about −21″ normal to the range

This leaves seven stations, forming two groups ranged near the 78° and 88ᵛ meridians respectively, which it will be convenient to take separately, on account of the differences in magnitude of the deflections in each, we have —

Station	Observed deflection in the meridian	Residual deflection normal to the range	Distance from main boundary
	″	″	
Eastern group—			
Kurseong	−46	−28	3 miles N
Siliguri	−18	− 7	12　„　S
Jalpaiguri	− 1	+ 7	33　„　S
Western group—			
Mussooree	−80	−16	4　„　N
Rajpur　.	−41	(−21)	0
Dehra Dun	−31	−15	6　„　S
Kahana	− 1	+ 2	50　„　S

The leading feature in these figures is the existence of a very large residual northerly deflection near the main boundary of the Himalayas, which decreases rapidly in a short distance on either side, and completely disappears at about 20 to 30 miles southwards   The hypothesis, in explanation of these facts, which has been offered by Colonel Burrard, is the existence of a belt of deficient density, of considerable depth, but of no great width, along the southern edge of the Himalayas   So long as this explanation was merely tentative and indicated as a possible hypothesis it largely escaped notice, but in the memoir referred to above some definite figures are given, 20 miles in depth is indicated, and, though no actual

* This figure agrees well enough with Colonel Burrard's estimate of −9″ as the effect of the attraction of masses within 5 miles of Rajpur, 'Survey of India,' 1901, Professional Paper No 5, p. 54.

figures are given, the context shows that the width is regarded as somewhere about 5 miles or less.   As the rift, postulated by Colonel Burrard, is on a scale of magnitude far in excess of anything for which there is geological precedent, I was led to investigate the evidence, to see whether some other explanation could not be found, more in accordance with geological observations   The investigation is not yet complete, but in the course of it I had occasion to study the effect which should result from the facts of geological structure along the southern margin of the range, so far as they are known, and the results of this study seem of sufficient interest, apart from their bearing on the general question of the geological interpretation of the geodetic observations, to be worth publishing

The facts of geological structure, so far as they need be considered, are very simple, and will be found, reduced to a diagrammatic form suitable for calculation, in the upper part of the diagram on p 473 of the 'Manual of the Geology of India'* Briefly expressed, they are as follows.—Along the southern edge of the Himalayas there is a great fault separating the older rocks of the range from the, upper tertiary, Siwalik beds, which were long ago shown by Mr. H B Medlicott† to have been formed under conditions similar to those of the recent deposits in the Gangetic depression, and to be, in fact, the lower, marginal, deposits of the same continuous formation, of which the Gangetic alluvium forms the uppermost members The depth of this formation, along the northern margin, cannot be stated with accuracy, and doubtless varies somewhat at different parts of the range, it is, however, certainly great, nowhere less than 10,000 feet, and possibly as much as 30,000 feet in places, though a more probable estimate lies between 15,000 and 20,000 feet   On the southern margin the thickness is small, and the deposit thins out over an old land surface of rock Between these two limits the form of the depression, occupied by the alluvium, cannot be determined by direct observation, but it is natural to suppose that the depth decreases gradually from north to south.

The density of the material filling this wedge-shaped depression can be determined within narrow limits, the lower is fixed at 1 8, being the density of the surface layers of the Gangetic alluvium, the upper at 2 2, being the density of the Siwaliks, which are the uplifted basal portion of the formation The mean density must lie between these limits, and, being probably nearer the higher than the lower, has been taken at 2 1,‡ the mean density of the

* 2nd edition, Calcutta, 1893
† 'Mem. Geol Surv Ind,' vol 3.
‡ These figures are taken from Colonel Burrard's memoir, and, having been obtained from the Geological Survey, may be accepted as authoritative.

rock forming the sides and floor of the depression being about 2 7   It is the effect of this large bulk of material, having a density of only about seven-ninths of the average density of surface rock, which has been investigated.

The method adopted was based on Mr Hayford's system of compartments * The trough was assumed to run east and west, with the deep side on the north. This is in approximate accordance with the conditions in the Gangetic depression and enables the deflections to be conveniently expressed in terms of the usual convention of the — sign for a northerly, and the + sign for a southerly, deflection.   To simplify calculation, the trough was divided into belts of 10 miles wide, running parallel to the margins, in each of which the depth was assumed to be uniform and equal to the mean depth of the belt, in other words, the lower surface of the depression was taken as a series of steps each 10 miles wide and gradually decreasing in depth below the surface from north to south   The number of compartments in each belt, multiplied by the depth and by the deficiency in density, gives the effective negative attraction, assumed to be concentrated at the surface.   For distances of over 10 miles from the station the error introduced by this assumption is negligible, but in the immediate vicinity of the station an important modification has to be introduced, owing to the fact that the defect in density is not concentrated at the surface, but distributed through a considerable vertical depth   The correction to be applied for this is easily obtained from Mr Hayford's data, on p 70 of his memoir he gives a series of factors to be applied to the attraction of visible masses, if they are compensated by a defect of density distributed uniformly through certain given depths, and on p 154 he gives a method by which the corresponding factors for any other depth may be obtained   Now these factors represent the difference between the positive attraction of the visible mass, taken as 1 0, and the negative attraction of the defect of density by which they are compensated, so that the latter can be obtained by simple subtraction, and is the factor required to reduce the calculated negative attraction of each column of deficient density to the horizontal plane   Actually these calculations were not gone through in every case, but the effect of the 10-mile belt of alluvium next the station was calculated for certain assumed depths, ranging up to 6 miles.   These were plotted on squared paper and a curve drawn through them, from which the effect, for any required depth, could be obtained by inspection, with sufficient accuracy for the purpose of this investigation.

As a standard, to represent approximately the average conditions, the depth of the depression, at its northern boundary, was taken as 3 5 miles and the

* J F Hayford, 'The Figure of the Earth and Isostasy, from Measurements in the United States,' Washington, 1909.

width as 100 miles, but further calculations were made, using larger and smaller values for each of these quantities, and from them the approximate effect of other assumed values may be readily obtained by interpolation or, reasonable, extrapolation

At the outset of my investigation I was only concerned with the difference of deflection as between two points about 10 miles apart and, as the effect of topography at over 50 miles from either would affect both almost equally, it was only necessary to consider the attraction of masses within that distance, these are the values which are given, to the nearest whole second of arc, in Tables I and II. The effect of including the attraction of masses within greater distances, and of introducing a compensation for isostasy, was also considered and is referred to below.

Table I —Deflections produced by a Trough of Alluvium of various widths, 3·5 miles deep at the northern boundary, 0 miles at the southern boundary Mean density of alluvium 2 1, of rock 2 7. Portions within 50 miles from stations only considered.

Distance from northern edge	Width of alluvium		
	70 miles	100 miles	140 miles
miles	"	"	"
40	− 2	− 2	− 2
30	− 3	− 3	− 3
20	− 6	− 6	− 6
10	−10	−11	−12
5	−14	−15	−16
0	−26	−28	−29
5	−11	−14	−15
10	− 5	− 7	− 9
20	+ 3	0	− 2
30	+ 7	+ 4	+ 2
40	+ 9	+ 6	+ 4
50	+10	+ 8	+ 6
60	+10	+ 8	+ 6
70	+ 8	+ 8	+ 6
80	+ 3	+ 8	+ 6
90	+ 1	+ 8	+ 6
100	0	+ 5	+ 6
110	0	+ 2	+ 6
120	0	+ 1	+ 6
130	0	0	+ 6
140	0	0	+ 4
150	0	0	+ 1

Table II—Deflections produced by a Trough of Alluvium, 100 miles in width, depth at the northern boundary as stated, 0 miles at the southern boundary   Mean density of alluvium 2 1, of rock 2 7.   Portions within 50 miles from station only considered

Distance from northern edge	Depth at northern boundary		
	5 25 miles	3 5 miles	1 75 miles
miles	"	"	"
50	0	0	0
40	− 2	− 2	− 1
30	− 5	− 3	− 2
20	− 9	− 6	− 3
10	−16	−11	− 5
5	−23	−15	− 8
0	−37	−28	−17
5	−20	−13	− 7
10	−11	− 7	− 3
20	− 1	0	0
30	+ 5	+ 4	+ 2
40	+ 9	+ 6	+ 3
50	+11	+ 8	+ 4
60	+11	+ 8	+ 4
70	+11	+ 8	+ 4
80	+11	+ 8	+ 4
90	+10	+ 8	+ 4
100	+ 8	+ 5	+ 3
110	+ 3	+ 2	+ 1
120	+ 1	+ 1	0
130	0	0	0
140	0	0	0
150	0	0	0

The values given in these tables include, as has been said, only the effect of masses within 50 miles of the stations; if this distance is extended to 100 miles, the deflections, in the case of a trough 3·5 miles deep at the northern margin and 100 miles broad, become—

					"
At 50 miles N. of the northern boundary . . .					− 4
„		„	„	.	−31
„ 50 „ S „			„		+ 9
„ 100 „ S „			,		+ 9
„ 150 „ S „			„	.	+ 1

The effect of a further extension of the distance is inappreciable for, even if the trough is assumed to extend for 1200 miles on either side of the station, the deflections at either boundary are only increased by 0·4″, and at 50 miles out by 0 5″, within the limits of the trough, the effect sinks to zero.

As so great a defect in mass may reasonably be expected to be compensated, in the same manner as is found in the case of mountain ranges, the effect of such compensation, assumed to be complete, was calculated, using Mr Hayford's factors, with the result that, all masses within 100 miles being considered, the resulting deflections became—

				"
At 50 miles N of the northern boundary				− 1
„	„	„		−24
„ 50 S	„	„	.	+ 5
„ 100 S	„	„		+ 4
„ 150 S	„	„	.	0

From these figures it will be seen that the nature of the effect is the same in every case, though the amount may vary, and that the effect of a depression, such as is occupied by the Gangetic alluvium, assuming its form to be such as has been independently determined from geological observation, would be to produce a large northerly deflection, amounting from 20″ to 30″, along the extreme edge of the Himalayas, a deflection which would almost disappear at about 50 miles to the northwards, and completely disappear at about 20 to 30 miles southwards, to be replaced by a southerly deflection from thence to, and for some distance beyond, the southern margin These deflections would be superimposed on those produced by the visible topography, and it will be noticed that they are of the same character as, and not materially different in magnitude from, the residuals, or unexplained deflections, shown in the figures given on p 34

For comparison with the results detailed above, it may be useful to consider the effect which would be produced by a deep and narrow rift, filled with matter of less density than the rock on either side, and, for the purpose of calculation, I have assumed a depth of 17 miles, a width of 5 miles, and a defect of density equal to one-ninth of the surrounding rock   With these data the deflections deduced are —

				"
At 20 miles north of the rift .		..	− 4
„ 10	„	„	..	− 5
„ 5	„	„	. . .	− 7
„ northern edge	„		−17
„ southern edge	„	.	.	+17
„ 5 miles south	„		. .	+ 7
„ 10	„	„	. .	+ 5
„ 20	„	„	. . . . .	+ 4

These figures will vary with any change in the adopted values of the dimensions, or of density of the matter filling the rift, but the general character of the curve will be unaltered. The greatest deflections will be at the edges of the rift, in opposite directions and away from the rift in either case, the amount of the deflection decreasing, without change of sign, with increasing distance from the rift in either direction

It will be noticed that, north of the Himalayan boundary, there would be no great difference in character between the curve deduced from this hypothesis and that which results from the geological structure, as generally accepted, but to the south of the boundary the difference would be radical
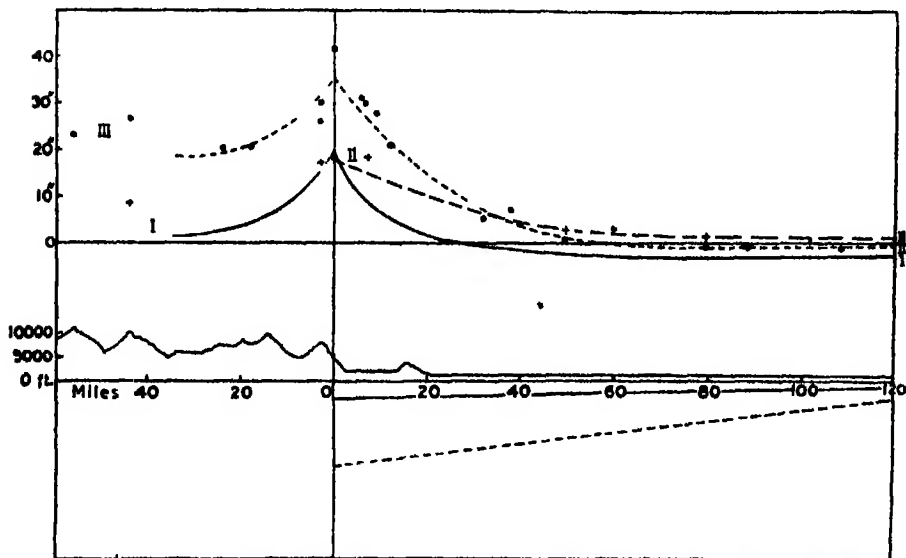
Fig 1 —Below is represented a generalised section across the outer Himalayas and Gangetic plain in about 88° E Long , the vertical scale exaggerated about five times   To the right, the general form of the Gangetic depression, as assumed for the purpose of calculation, is indicated, to the same vertical scale, by the dotted line, and the equivalent deficiency of mass, expressed as rock of the average density of the range, by the firm line

Above are shown curves of, I, deflections due to the defect of mass in the Gangetic depression, converted into the meridian ; II, of the calculated effect of visible topography, assumed to be compensated for isostasy, as determined by Major Crosthwait , and, III, of the observed deflection of the plumb-line   It will be noticed that, in the region near and to the south of the main Himalayan boundary, the Curve III is closely concordant with the combined effects of I and II ; northwards of the main boundary data for comparison are wanting

Round dots represent observed deflections , crosses, the, compensated, effect of visible topography.

Distances are measured normal to the general direction of the range , deflections in the meridian

On the hypothesis of a rift the southerly residual should be greatest close to the boundary, and decrease with increasing distance, whereas the residual deflections actually continue to have a northerly sign till a distance of 20 to 30 miles is reached, and then a southerly sign, increasing in amount with an increase of distance from the Himalayas

The general conclusions to be drawn from these investigations seem to be twofold (1) that the local deflections of the plumb-line, produced by underground topography, along the region bordering the southern margin of the Himalayas, are of such magnitude as to make the observations, at stations situated in that region, of small geodetic value, unless allowance is made for the invisible, as well as the visible, topography, and (2) that there is no geodetic justification for the assumption of the existence of a deep and narrow rift, filled with material of lesser density than the rock on either side, or for any modification of the deductions, regarding the form of the floor of the Gangetic depression, which have been drawn from geological observation

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Note on Osmotic Pressure.

By W R. BOUSFIELD, M A , K C

The vapour pressure theory regards osmotic pressure as the pressure required to produce equilibrium between the pure solvent and the solution. Pressure applied to a solution increases its internal vapour pressure If the compressed solution be on one side of a semi-permeable partition and the pure solvent on the other, there is osmotic equilibrium when the compression of the solution brings its vapour pressure to equality with that of the solvent So long ago as 1894 Ramsay* found that with a partition of palladium, permeable to hydrogen but not to nitrogen, the hydrogen pressures on each side tended to equality, notwithstanding the presence of nitrogen under pressure on one side, which it might have been supposed would have resisted the transpiration of the hydrogen. The bearing of this experiment on the problem of osmotic pressure was recognised by van't Hoff, who observes† that "it is very instructive as regards the means

* 'Phil. Mag.,' vol. 38, p. 206 (1894).

† Van't Hoff, 'Lectures on Theoretical and Physical Chemistry,' Part II, p. 38.

by which osmotic pressure is produced." But it was not till 1908 that the vapour pressure theory of osmotic pressure was developed on a firm foundation by Callendar * He demonstrated, by the method of the "vapour sieve" piston, the proposition that "any two solutions in equilibrium through any kind of membrane or capillary surface must have the same vapour pressures in respect of each of their constituents which is capable of diffusing through their surface of separation"—a generalisation of great importance for the theory of solutions Findlay, in his admirable mono-graph,† gives a very complete account of the contending theories of osmotic pressure, a review of which leaves no doubt that at the present moment the vapour pressure theory stands without a serious rival. Some confusion of ideas still arises from the want of adherence to a strict definition of osmotic pressure to which numerical data from experimental measurements should be reduced The following definitions appear to be the outcome of the vapour pressure theory —

Definition I—The vapour pressure of a solution is the pressure of the vapour with which it is in equilibrium when under pressure of its own vapour only

Definition II—The osmotic pressure of a solution of given uniform concentration at a given temperature is the pressure under which the internal vapour pressure of such solution becomes equal to the vapour pressure of the pure solvent at the same temperature and under the pressure of its own vapour only.

From these definitions it would follow that for a given concentration and temperature the vapour pressure and osmotic pressure of a solution would be definite physical quantities determined only by temperature and concen-tration, and such confusing phrases as "the variation of osmotic pressure with hydrostatic pressure" or "the osmotic pressure at the top of a column of solution" would fall into desuetude. The picturesque conception of van't Hoff, that the osmotic pressure of a solution is the pressure which would be produced if the solute existed as a gas in the same space, has sometimes been taken too literally, and is probably responsible for the survival of some inexact phraseology

Both Callendar and Findlay appear to regard the compressibility of the solvent as a factor which need only be reckoned with at very high pressures, or as introducing into the expression of the relation between vapour pressure and osmotic pressure a term of minor importance, which needs to be considered merely as a correction where a closer approximation is required.

* 'Roy Soc Proc.,' A, vol. 80, p. 466 (1908).
† 'Osmotic Pressure,' Longmans, Green, and Co, 1913.

But it is the compression of the solution which produces the increase of its vapour pressure and if we look at the matter from the point of view of the reduction of the molecular interspaces which is produced by pressure, it is seen that the compression of the solution may possibly play a fundamental *rôle*

The complex constitution of liquid water has created many difficulties for physicists in dealing with aqueous solutions, but it may in this matter give us a useful idea

It has been shown elsewhere* that liquid water is probably a mixture of ice-molecules of a constitution $(H_2O)_3$, dihydrol $(H_2O)_2$, and steam-molecules H_2O The proportions of these ingredients vary with temperature Near the freezing-point there is a large proportion of ice-molecules and a small proportion of steam-molecules   Near the boiling point these proportions are reversed   We may well suppose that the vapour pressure of water is intimately connected with the proportion of steam-molecules which it contains at any given temperature   There is also little doubt that the proportion of steam-molecules (as well as of ice-molecules) is reduced by the solution in water of any solute, and that this is connected with the reduction of vapour pressure which is thus produced   In another paper† the remarkable fact was pointed out that steam-molecules, like ice-molecules, must be considered as bulky molecules, that is, as occupying a larger volume in the solution than their weight would entitle them to In the case of the ice-molecule this may be attributed to its more open structure.   In the case of the compact steam-molecule it may well be attributed to the larger space which it requires for its vibratory movement We thus get the idea of molecular interspaces containing steam-molecules or vapour which determine the internal vapour pressure of the liquid

When a mass of vapour is in external contact with a solution and the space in which the vapour is confined is reduced, vapour is condensed, and no change of pressure is produced   But the conditions in the molecular interspaces of the solvent are different, and it is easy to show that the assumption that the molecular interspaces are filled with vapour (steam-molecules), which there behaves approximately as a perfect gas, leads at once to the known general relation between vapour pressure and osmotic pressure

If P be the pressure in atmospheres applied to a litre of solution, the change of volume produced by such pressure may be expressed approximately as

$$\delta V = aP.$$

Let p be the vapour pressure of water and $p - \delta p$ the vapour pressure of a

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* Bousfield and Lowry, "Liquid Water a Ternary Mixture," 'Farad. Soc. Trans.,' 1910.

† Bousfield and Lowry, 'Phil Trans,' A, vol 204, p 283 (1905)

solution at the same temperature   Let V_0 be the initial molecular inter-space in a litre of the solution under no pressure except that of its own vapour   Let the solution be now compressed to a pressure equal to its osmotic pressure P   Its volume will be reduced by an amount δV, so that the interspace volume is reduced to $V_0 - \delta V$, whilst its internal vapour pressure is increased from $p - \delta p$ to p Then, assuming that the interspace vapour may be treated as a perfect gas, we have

$$(p - \delta p)\, V_0 = p\,(V_0 - \delta V) \quad \text{or} \quad V_0 \delta p = p\delta V,$$

and since $\delta V = a\mathrm{P}$, we get

$$\mathrm{P} = \frac{V_0}{a}\,\frac{\delta p}{p}$$

If we compare this with the approximate thermodynamical result

$$\mathrm{P} = \mathrm{R}'\mathrm{T}\rho\,\frac{\delta p}{p},$$

we see that our theory requires that the initial value of the interspace per litre of solution should be

$$V_0 = a\mathrm{R}'\mathrm{T}\rho$$

Since $\mathrm{R}' = 0\,0821 \times 1000/18 = 4\,557$, and $a = 0\,00005$ (taking the approximate value for water), the required interspace upon the above view is about 66 c c per litre at 15° C

The conception that the vapour in the molecular interspaces of a solution behaves on compression of the solution approximately as a perfect gas thus leads to the same general result as that which is derived from thermodynamical considerations.   It furnishes a mental picture which may be compared with van't Hoff's analogy of the solute behaving as if it were approximately a perfect gas existing in the space in which it is dissolved. But the conception that the solute behaves as a perfect gas may lead to a mode of thought and a phraseology which are incorrect, whilst the con-ception that the vapour within the solution behaves as a perfect gas leads to a mode of thought and language which are strictly in accordance with the vapour pressure theory of osmotic pressure

In arriving at the result given above the assumptions made are of about the same order of inexactitude as those by which the approximate thermo-dynamical expression is reached.

The fundamental assumptions are that the molecular interspace is reduced by an amount equal to the total reduction of volume by compression, and that the number of steam-molecules existing in the interspace is unaltered by compression.   If the molecules and atoms are themselves compressible the interspace would be reduced by a less amount than δV, but if the relative reductions were in a constant ratio this would not affect the

character of the result   The more serious matter is that compression does affect the proportions of the molecular varieties existing in water, especially at low temperatures and in dilute solutions.   It was shown in the paper to which reference has been made that with increasing concentration there is simplification of an aqueous solution which is probably due to " the destruction of the ice-molecules to which water owes most of its abnormal properties "   But in a dilute solution near 0° C we have to reckon seriously with the ice-molecules.   As a matter of fact Morse and his co-workers* have observed a well marked abnormality in the value of the osmotic pressure of a decinormal sucrose solution at 0° C

The efficiency of hydrostatic pressure in increasing vapour pressure in a dilute solution near the freezing-point is difficult to estimate   The compressibility of water rises as we approach the freezing-point   There the number of ice-molecules is greatest, and they are probably destroyed by compression in large numbers.   The molecular varieties into which these bulky ice-molecules are changed must have a less mean specific volume than the ice-molecules   This probably means that the reaction due to pressure is more nearly

$$2\,(H_2O)_3 = 3\,(H_2O)_2 \quad \text{than} \quad (H_2O)_3 = (H_2O)_2 + H_2O$$

Since the reduction of volume due to this change would not seriously affect the molecular interspace volume, the efficiency of hydrostatic pressure in producing change of vapour pressure would in this way be reduced near the freezing-point   On the other hand, any generation of steam-molecules from the broken down ice-molecules would tend to increase such efficiency

Morse and his co-workers state that they have given special care to determining the osmotic pressure of their most dilute sucrose solution at 0° C   They state that the osmotic pressure is actually greater at 0° C. than at 5° C   If this result can be relied upon it seems to show that the efficiency of hydrostatic pressure in producing a rise of vapour pressure at the freezing-point is abnormally low   The abnormality, however, seems to disappear at twice decinormal concentration.

Whilst our theoretical deductions as to the nature of solutions which are derived from conductivity data must at present be based on dilute solutions, the reverse is the case with deductions from data as to osmotic pressures   Fortunately at higher concentrations and temperatures the ice-molecules, whose sensitiveness to pressure disturbs osmotic measurements, practically disappear, and the aqueous solvent becomes approximately a simple binary mixture of $(H_2O)_2$ and H_2O

* Morse, Holland, Zies, Myers, Clark, and Gill, ' Amer Chem Journ.,' vol 45, p 502 (1911).

On the Formula for Black Body Radiation.

By George W. Walker, A R C Sc, M.A, F R S, formerly
Fellow of Trinity College, Cambridge

In a recent paper[*] I showed that the experimental data with regard to "black body" radiation could be represented exceedingly well by an empirical formula for the radiation function at temperature θ, and wavelength λ, viz.,—

$$\phi(\theta, \lambda) = k\theta^5 \left\{ \frac{\lambda\theta}{\lambda^2\theta^2 + a^2} \right\}^4$$

I further indicated an electric system which gives rise to an emission function which is a generalised form of the above empirical expression

It is a matter of interest to see if one can learn more as to the character of a system which would give the empirical form precisely The method of doing so by Fourier analysis was indicated by Lord Rayleigh[†]

The form of the primary disturbance which leads to the above spectral distribution of energy is found to be very simple, and almost suggests itself

If we take a function ψ of the time t such that

$$\psi(t) = t\epsilon^{-n_0 t} \quad \text{for} \quad \infty > t > 0,$$
$$= t\epsilon^{n_0 t} \quad \text{for} \quad 0 > t > -\infty,$$

then the Fourier representation of the function is

$$\psi(t) = \frac{4 n_0}{\pi} \int_0^\infty \frac{n \sin nt}{(n^2 + n_0^2)^2} \delta n,$$

and, further, for a number of arbitrary disturbances of this type we get

$$\int_{-\infty}^{+\infty} \{\psi(t)\}^2 dt = \frac{16 n_0^2}{\pi} \int_0^\infty \frac{n^2}{(n^2 + n_0^2)^4} \delta n$$

The spectral distribution of $\{\psi(t)\}^2$ is thus of the form $\dfrac{n_0^2 n^2}{(n^2 + n_0^2)^4} \delta n$, and since n varies as λ^{-1}, we thus get the empirical form as far as λ enters

The further interpretation of the formula now depends, as regards detail, upon whether we proceed in terms of pure dynamics or electro-dynamics In the first case we should regard $\psi(t)$ as proportional to the velocity of displacement, and in the second as proportional to the acceleration of the

[*] 'Roy Soc Proc,' A, vol. 89, p. 393 (1913)

[†] 'Phil Mag,' vol 27, p. 460 (1889)

displacement   But in either case the radiation between frequency n and $n + \delta n$ will be expressed by

$$m\mathrm{A}^2 \frac{n_0^2 n^2}{(n^2 + n_0^2)^4} \delta n,$$

where A is a quantity defining the amplitude of the disturbance, and m is the number of such disturbances per second

In order to obtain Wien's displacement law n_0 must vary as θ, and then further we get Stefan's law if $m\mathrm{A}^2$ varies as θ^7, and the formula reduces to the empirical form

$$\lambda \theta^5 \left\{ \frac{\lambda \theta}{\lambda^2 \theta^2 + a^2} \right\}^4 \delta \lambda$$

The important point we have obtained is that, in order to have this energy distribution, the primary type of disturbance required is a solution of the equation

$$x + 2 n_0 \dot{x} + n_0^2 x = 0,$$

which expresses the motion of an aperiodic dynamical system   Further, n_0 must be proportional to θ But the present analysis does not indicate how this occurs, nor how m and A separately depend on temperature

The primary type of disturbance can also arise as a solution of electro-dynamic equations. Such an interpretation raises points of importance which I have not yet had opportunity to consider fully

Appendix   [*Added January 29th,* 1914]

In response to requests from several quarters as to the agreement between the formula and the data, I add the following information which I have been able to obtain.

If we choose the constants in Planck's formula and my own so that they give the same value for Wien's constant $a = \lambda_m \theta$ and so that they agree at the maximum, we get the following table —

λ/λ_m	Planck.	Walker
0·0	0·0	0·0
0·25	0·0004	0·0490
0·333	0·0117	0·1292
0·5	0·2217	0·4096
0·666	0·6302	0·7260
1·0	1·0	1·0
2·0	0·4054	0·4096
3·0	0·1394	0·1292
4·0	0·0564	0·0490
10·0	0·0022	0·0015
∞	0·0	0·0

The two curves are shown in the figure.
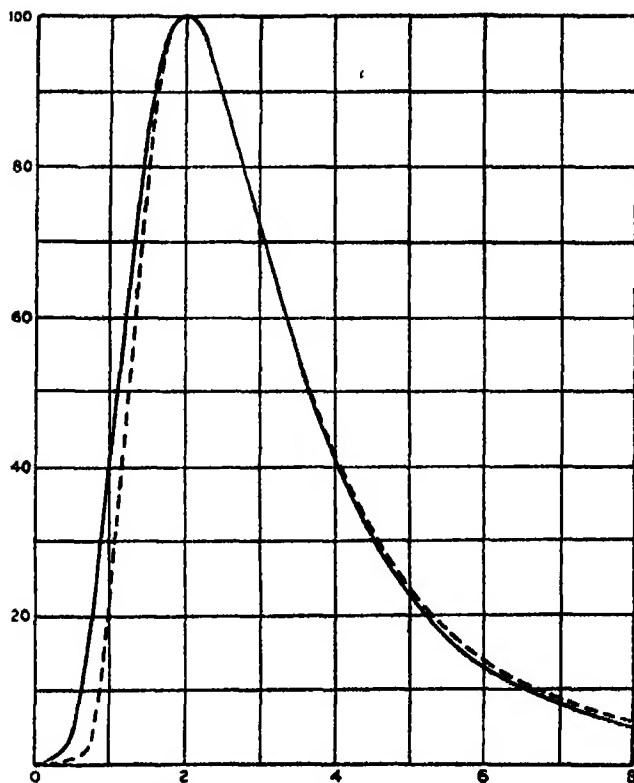
Interrupted line—Planck's curve   Continuous line—Walker's curve

The ordinates by Planck's formula are less than those by my formula for $\lambda/\lambda_m < 1$ and greater than mine when $\lambda/\lambda_m > 1$ But the area of the whole curves I find to be the same to 3 per cent

Passing to the data, it is clearly not easy to discriminate between the formula within small ranges of wave-length.   Thus Warburg's recent work,[*] within a range of about $1\,\mu$, is not of much assistance.   I have had to go back to the older measurements.

Lummer and Pringsheim[†] give a curve of emission for $\theta = 1650°$ absolute from $\lambda = 0\,5\,\mu$ to about $18\,\mu$.   I find that it lies almost exactly between the two theoretical curves, the advantage being very slightly in favour of my own formula

Paschen[‡] finds very good agreement with Planck's formula for any one wave-length at different temperatures, but he explains that in order to fit

* 'Ann d Phys,' 1913, p. 613
† 'Verh d Deutsch Phys. Gesell.,' 1900, p. 177
‡ 'Ann d Phys,' vol 4, p. 277 (1901).

Planck's formula over his range from about $1\,\mu$ to $9\,\mu$ he requires to assume that for "some unknown cause" the spectrum is weakened in passing to increasing wave-lengths, and that the observed values must be multiplied by increasing factors, the factor at $9\,\mu$ being $1\,3$, I understand, as compared with 1 at $1\,\mu$. This is hardly convincing proof, and the facts suggest that my formula would avoid the necessity for these factors.

Rubens'[*] values for long waves up to $50\,\mu$ are relative and give good agreement with any formula that converges to Lord Rayleigh's form. If, however, we could compare the values for long waves with those at $1\,\mu$, we have a means of deciding between the two formulæ as follows

Writing Planck's formula in the form

$$k\,(4\,9651\,a)\,\lambda^{-5}/(e^{4\,9651\,a/\lambda\theta}-1),$$

we get the comparative table—

	Planck	Walker
Maximum occurs when	$\lambda_m\theta = a$	$\lambda_m\theta = a$
Total radiation is	$0\,0580\,k\theta^4 a^{-3}$	$0\,0982\,k\theta^4 a^{-3}$
Maximum radiation is	$0\,0848\,k\theta^5 a^{-4}$	$0\,0625\,k\theta^5 a^{-4}$
Value for long waves	$k\theta\lambda^{-4}$	$k\theta\lambda^{-4}$

Thus, if we chose k in each formula so as to get the total radiation or (as it happens) the maximum radiation to agree, then Planck's ordinates for long waves would be $1\,8$ times the ordinates from my formula

It is worth while to note that it must be rather difficult to determine the maximum wave-length accurately The table suggests that we could get a independently and hence λ_m for any temperature by comparing the total and the maximum radiation Both formulæ would give the same value for a to 3 per cent.

[*] 'Ann d Phys,' 1901, vol 4, p 649

The Transmission of Electric Waves around the Earth's Surface.

By Prof H M MACDONALD, F R.S

In a previous communication,[*] an expression for the magnetic force at any point when a Hertzian oscillator is placed outside a perfectly conducting sphere was obtained, and the principal parts of this were evaluated, in particular it was found that when the point is inside the geometrical shadow and at an angular distance from the line of contact of the shadow with the surface which is of higher order than $(\kappa a)^{-\frac{1}{3}}$, the ratio of the magnetic force to the magnetic force due to the oscillator alone is a Gilbert integral, when the point and the oscillator both approach the surface this integral tends to zero, but it may be expected to give information as to the way the magnetic force dies away in the neighbourhood where it has diminished to order $(\kappa a)^{-\frac{1}{3}} \psi_1$.

The magnetic force on the surface when the oscillator is also on the surface was reinvestigated by Poincaré,[†] and he indicated that the magnetic force at angular distance θ from the oscillator is of the form $A r^{-\alpha \theta}$, where A and α depend on the zero of $\dfrac{\partial}{\partial z_0} \{ z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) \}$, for which $|n + \frac{1}{2} - z_0|$ is least   The value of this zero was calculated by Nicholson,[‡] who also calculated the value of A   The value given[§] by him does not agree with the coefficient of the corresponding term in the series found below, this may be due to the fact that the process of summation employed by him is invalid as it assumes that $z^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z) \Big/ \dfrac{\partial}{\partial z} \{ z^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z) \}$ is a meromorphic function of $n + \frac{1}{2}$, which is not true   The problem has recently been discussed by March[||] and Rybczynski[¶], the discussion in the second of these papers is very interesting, but the singularity of the integrand which contributes ultimately alone to the result is one which appears to have been introduced in the process, and which is not a singularity of the original expression for which the integrand is an approximation   The author remarks on the impossibility of representing the facts by a single exponential as the oscillator is approached , this is fully borne out below

[*] 'Phil Trans.,' A, vol 210, p 113 (1909)
[†] 'Rendiconti Palermo,' vol 29 (1910).
[‡] 'Phil Mag,' 1911
[§] 'Phil Mag,' April, 1910
[||] 'Ann. der Phys.,' vol 37
[¶] 'Ann der Phys,' vol 41.

In what follows a series is obtained which represents the magnetic force at any point on the surface when the oscillator is also on the surface, the series converges rapidly for large values of θ, and for large values the first term is a sufficient approximation For small values of θ the series converges very slowly Tables showing the fall in amplitude with increase of distance have been calculated for different wave-lengths

The magnetic force γ at a point P, whose distance from the centre of the sphere is r, and whose angular distance from the oscillator is θ, is given by

$$\gamma r \sin \theta = \psi e^{\iota \kappa V t},$$

$$\psi = -r_1^{-\frac{1}{2}} r^{\frac{1}{2}} \sum_1^\infty e^{\frac{1}{2}(n+\frac{1}{2})\pi \iota} (2n+1) K_{n+\frac{1}{2}}(\iota \kappa r_1) \left[J_{n+\frac{1}{2}}(\kappa r) - \frac{\dfrac{\partial}{\partial a}\{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\}}{\dfrac{\partial}{\partial a}\{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota \kappa a)\}} K_{n+\frac{1}{2}}(\kappa r) \right.$$

$$\left. \times (1-\mu^2)\frac{dP_n}{d\mu}, \quad r_1 > r > a, \right.$$

where r_1 is the distance of the oscillator from the centre of the sphere, a is the radius of the sphere, $2\pi/\kappa$ is the wave-length of the oscillations, and $\mu = \cos \theta$ Writing

$$\kappa a = z_0, \qquad \kappa r_1 = z_1, \qquad \kappa r = z,$$

this becomes

$$\psi = -\kappa z_1^{-\frac{1}{2}} \sum_1^\infty e^{\frac{1}{2}(n+\frac{1}{2})\pi \iota} (2n+1) z_1^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z_1) \left[z^{\frac{1}{2}} J_{n+\frac{1}{2}}(z) - \frac{\dfrac{\partial}{\partial z_0}\{z_0^{\frac{1}{2}} J_{n+\frac{1}{2}}(z_0)\}}{\dfrac{\partial}{\partial z_0}\{z_0^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z_0)\}} \right.$$

$$\left. \times z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) \right](1-\mu^2)\frac{\partial P_n}{\partial \mu}. \quad (1)$$

It has been proved that, when the point P is outside the boundary of the geometrical shadow and on the side of the sphere remote from the oscillator, the principal part of ψ is contributed by two sets of terms of the series (1), where the rate of oscillation of the series is small, for one of these sets of terms the values of n are less than z_0, and for the other set the values of n are greater than z_0 As the point P approaches the boundary of the geometrical shadow, the values of n for which the rate of oscillation of the series vanishes both approach z_0, and therefore, when the point P is near to the boundary of the geometrical shadow or inside it, the principal part of the series is contributed by the terms for which n is in the neighbourhood of z_0.

For the special case, where the point P is on the surface, since

$$e^{\frac{1}{2}(n+\frac{1}{2})\pi \iota} \left[z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) \frac{\partial}{\partial z}\{z^{\frac{1}{2}} J_{n+\frac{1}{2}}(z)\} - z^{\frac{1}{2}} J_{n+\frac{1}{2}}(z) \frac{\partial}{\partial z}\{z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z)\} \right] = 1,$$

the relation (1) becomes

$$\psi = \kappa z_1^{-\frac{3}{2}} \sum_{1}^{\infty} (2n+1) \frac{z_1^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z_1)}{\frac{\partial}{\partial z_0} \{z_0^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z_0)\}} (1-\mu^2) \frac{dP_n}{d\mu} \tag{2}$$

The sum of the terms of this series, for which $n+\frac{1}{2}-z_0$ is of higher order than $z_0^{\frac{1}{2}}$, is at most of the order $z_0^{-\frac{1}{2}}\psi_1$, where ψ_1 is the value of ψ at the point P due to the oscillator alone,* the sum of the terms of the series for which $z_0-n-\frac{1}{2}$ is of higher order than $z_0^{\frac{1}{2}}$ is also at most of the order $z_0^{-\frac{1}{2}}\psi_1$, for ϕ_0 can be expressed in the form $z_0 \sum_0 b_m z_0^{-m}$ in the neighbourhood of any such term   Hence the terms of the series (2) which are important are those for which $|n+\frac{1}{2}-z_0|$ is of the same or of lower order than $z_0^{\frac{1}{2}}$ Now, when $|n+\frac{1}{2}-z|$ is of the same or of lower order than $z^{\frac{1}{2}}$, $z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z)$ to the order of approximation required satisfies the differential equation†

$$\frac{d^2 w}{d\zeta^2} - 9\zeta w = 0,$$

where $\qquad\qquad 3\zeta = 6^{\frac{1}{3}} z^{-\frac{1}{3}}(n+\frac{1}{2}-z),$

writing $\qquad\qquad \xi = 2\zeta^{\frac{3}{2}},$

this differential equation becomes

$$\frac{d^2 w}{d\xi^2} + \frac{1}{3\xi} \cdot \frac{dw}{d\xi} - w = 0,$$

the solution of which is

$$w = \xi^{\frac{1}{3}}[A I_{\frac{1}{3}}(\xi) + B I_{-\frac{1}{3}}(\xi)],$$

where I_n is Bessel's function with imaginary argument

Again,† to the same order of approximation,

$$z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) = 6^{\frac{1}{3}}\pi^{-1} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota} \sum_{k=0}^{\infty} \{1 + e^{\frac{1}{3}(2k-1)\pi\iota}\} \frac{1}{3}(3\zeta)^k \frac{\Gamma\{\frac{1}{3}(k+1)\}}{\Gamma(k+1)},$$

therefore

$$2^{\frac{1}{3}} B \frac{1}{\Gamma(\frac{2}{3})} = 6^{\frac{1}{3}}\pi^{-1} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota}(1 + e^{-\frac{1}{3}\pi\iota})\frac{1}{3}\Gamma(\frac{1}{3}),$$

$$2^{\frac{1}{3}} A \frac{1}{\Gamma(\frac{4}{3})} = 6^{\frac{1}{3}}\pi^{-1} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota}(1 + e^{\frac{1}{3}\pi\iota})\Gamma(\frac{2}{3}),$$

that is

$$B = 2 \ 3^{-\frac{1}{2}} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota - \frac{1}{6}\pi\iota}, \qquad A = 2 \ 3^{-\frac{1}{2}} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota + \frac{1}{6}\pi\iota},$$

and

$$z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) = 2 \ 3^{-\frac{1}{2}} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota} \xi^{\frac{1}{3}}[e^{-\frac{1}{6}\pi\iota} I_{-\frac{1}{3}}(\xi) + e^{\frac{1}{6}\pi\iota} I_{\frac{1}{3}}(\xi)],$$

or

$$z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) = \frac{2}{\pi} 3^{-\frac{1}{2}} z^{\frac{1}{2}} e^{-\frac{1}{2}(n+\frac{1}{2})\pi\iota} \xi^{\frac{1}{3}} K_{\frac{1}{3}}(\xi e^{-\pi\iota}). \tag{3}$$

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* 'Phil Trans.,' A, vol. 210, p. 117
† 'Phil Trans.,' A, vol 210, p. 136

Further $\qquad \dfrac{\partial}{\partial z}\{z^{\frac{1}{3}}K_{n+\frac{1}{3}}(\iota z)\} = -3^{\frac{1}{3}}z^{-\frac{1}{3}}\xi^{\frac{1}{3}}\dfrac{\partial}{\partial\xi}\{z^{\frac{1}{3}}K_{n+\frac{1}{3}}(\iota z)\},$

that is

$$\frac{\partial}{\partial z}\{z^{\frac{1}{3}}K_{n+\frac{1}{3}}(\iota z)\} = -3^{\frac{1}{3}}z^{-\frac{1}{3}}\xi^{\frac{1}{3}}\frac{\partial}{\partial\xi}\left\{\frac{2}{\pi}\,3^{-\frac{1}{3}}z^{\frac{1}{3}}e^{-\frac{1}{3}(n+1)\pi\iota}\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})\right\},$$

whence $\qquad \dfrac{\partial}{\partial z}\{z^{\frac{1}{3}}K_{n+\frac{1}{3}}(\iota z)\} = -\dfrac{2}{\pi}\,3^{\frac{1}{3}}z^{-\frac{1}{3}}e^{-\frac{1}{3}(n+1)\pi\iota}\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$

A knowledge of the zeros of $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ is required for the treatment of the series (2), and these will now be discussed The function $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ is an integral function of $\xi^{\frac{2}{3}}$, and therefore what is required is the values of $\xi^{\frac{2}{3}}$ for which it vanishes Since $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ is unaltered when $\xi e^{3\pi\iota}$ is written for ξ, it will be sufficient to consider values of ξ whose arguments lie between 0 and 3π, now $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi)$ has no zeros whose moduli are finite when the argument of ξ is greater than $-\frac{1}{2}\pi$ and less than $\frac{1}{2}\pi$,[*] therefore $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ has no zeros whose moduli are finite and whose arguments are greater than $\frac{1}{2}\pi$ and less than $\frac{3}{2}\pi$ When the argument of ξ lies between 0 and $\frac{1}{2}\pi$, writing $\xi = \xi'e^{\frac{1}{2}\pi\iota}$,

$$K_{\frac{1}{3}}(\xi e^{-\pi\iota}) = K_{\frac{1}{3}}(\xi'e^{-\frac{1}{2}\pi\iota}),$$

that is $\qquad\qquad K_{\frac{1}{3}}(\xi e^{-\pi\iota}) = K_{\frac{1}{3}}(-\iota\xi'),$

which has no zeros whose arguments lie between $-\frac{1}{2}\pi$ and $\frac{1}{2}\pi$ and whose moduli are finite When the argument of ξ lies between $\frac{1}{2}\pi$ and 3π, writing $\xi = \xi'e^{\pi\iota}$,

$$K_{\frac{1}{3}}(\xi e^{-\pi\iota}) = K_{\frac{1}{3}}(\xi'e^{\pi\iota}),$$

that is $\qquad K_{\frac{1}{3}}(\xi e^{-\pi\iota}) = \dfrac{\pi}{2\sin(2\pi/3)}[J_{-\frac{1}{3}}(\xi')-J_{\frac{1}{3}}(\xi')].$

Hence the zeros of $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ are the values of $\xi^{\frac{2}{3}}$ that correspond to the real values of $\xi'^{\frac{2}{3}}$ that satisfy the relation

$$J_{-\frac{1}{3}}(\xi')-J_{\frac{1}{3}}(\xi') = 0$$

Now $\qquad\qquad J_{-n}(x) = e^{n\pi\iota}J_n(x)+\dfrac{2}{\pi}\sin n\pi e^{\frac{1}{2}n\pi\iota}K_n(\iota x),$

and $\qquad\qquad J_n(x) = \dfrac{(2\pi x)^{-\frac{1}{2}}}{\Gamma(n+\frac{1}{2})}[e^{\iota x-\frac{1}{2}(2n+1)\frac{1}{2}\pi\iota}W_1 + e^{-\iota x+\frac{1}{2}(2n+1)\frac{1}{2}\pi\iota}W_2],$

$$K_n(x) = \dfrac{\pi^{\frac{1}{2}}(2x)^{-\frac{1}{2}}}{\Gamma(n+\frac{1}{2})}e^{-\iota x-\frac{1}{2}n\pi}W_2,$$

where

$$W_1 = \int_0^\infty e^{-s}s^{n-\frac{1}{2}}\left(1+\frac{\iota s}{2x}\right)^{n-\frac{1}{2}}ds, \qquad W_2 = \int_0^\infty e^{-s}s^{n-\frac{1}{2}}\left(1-\frac{\iota s}{2x}\right)^{n-\frac{1}{2}}ds,$$

[*] Macdonald, 'Lond. Math Soc. Proc.,' vol 30, p. 173 (1899)

therefore

$$J_{-n}(v) - J_n(x) = \frac{(2\pi x)^{-\frac{1}{2}}}{\Gamma(n+\frac{1}{2})}[(e^{n\pi \iota}-1)\{e^{\iota x - \frac{1}{4}(2n+1)\pi \iota}W_1 + e^{-\iota x + \frac{1}{4}(2n+1)\pi \iota}W_2\}$$
$$+ 2\sin n\pi \, e^{-\iota x + \frac{1}{4}(2n-1)\pi \iota}W_2],$$

that is

$$J_{-n}(x) - J_n(x) = \frac{(2\pi \iota)^{-\frac{1}{2}}}{\Gamma(n+\frac{1}{2})}(e^{n\pi \iota}-1)[e^{\iota x - \frac{1}{4}(2n+1)\pi \iota}W_1 - e^{-\iota x - \frac{1}{4}(2n+1)\pi \iota}W_2],$$

or

$$J_{-n}(x) - J_n(x) = 2\iota(2\pi x)^{-\frac{1}{2}}\sin \tfrac{1}{2}n\pi \frac{1}{\Gamma(n+\frac{1}{2})}[e^{\iota x - \frac{1}{4}\pi \iota}W_1 - e^{-\iota x + \frac{1}{4}\pi \iota}W_2]$$

Therefore the zeros of $J_{-\frac{1}{3}}(x) - J_{\frac{1}{3}}(x)$ are the real values of $x^{\frac{1}{3}}$ which satisfy the relation

$$e^{2\iota x - \frac{1}{2}\pi \iota} = W_2'/W_1',$$

where $\qquad W_1' = \int_0^\infty e^{-s_3\iota}\left(1 + \frac{\iota s}{2x}\right)^{\frac{1}{3}}ds, \qquad W_2' = \int_0^\infty e^{-s_3\iota}\left(1 - \frac{\iota s}{2x}\right)^{\frac{1}{3}}ds$

The values of x which satisfy the above are given by the relation

$$x_k = (k+\tfrac{1}{4})\pi + \frac{1}{2\iota}\log\frac{W_2'}{W_1'},$$

where k is any positive integer including zero, that is by the relation

$$x_k = (k+\tfrac{1}{4})\pi - \tan^{-1}\frac{U}{V}, \tag{4}$$

where $\qquad\qquad 2\iota U = W_1' - W_2', \qquad 2V = W_1' + W_2'$

Hence the values of $\xi^{\frac{1}{3}}$, which are zeros of $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi \iota})$ are given by $x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi \iota}$, where $x_k^{\frac{1}{3}}$ is the real cube root of x_k and x_k is determined by the relation (4).

The corresponding values of ζ are given by $2^{-\frac{1}{3}}x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi \iota}$, for

$$\xi = 2\zeta^{\frac{1}{3}},$$

For the calculations in view a fairly accurate value of x_0 is required, and only a rough approximation for x_1 The relation (4) is unsuitable for the evaluation of x_0, but it can readily be obtained from the relation

$$J_{-\frac{1}{3}}(x) - J_{\frac{1}{3}}(x) = 0,$$

and its value to four places of decimals is 0·6854. Approximations for the next two zeros are $x_1 = 3\,90$, $x_2 = 7\,05$, the remaining zeros can be obtained very accurately from the relation (4)

For the special case where the oscillator is very near to the surface, z_1 can be taken to be equal to z_0 except for points very near to the oscillator, and the relation (2) then becomes

$$\psi = \kappa z_0^{-\frac{3}{2}}\sum_1^\infty (2n+1)\frac{z_0^{\frac{1}{2}}K_{n+\frac{1}{2}}(\iota z_0)}{\frac{\partial}{\partial z_0}\{z_0^{\frac{1}{2}}K_{n+\frac{1}{2}}(\iota z_0)\}}(1-\mu^2)\frac{dP_n}{d\mu}.$$

Since the important terms of the series are those for which $|n+\tfrac{1}{2}-z_0|$ is of the same or of lower order than $z_0^{\frac{1}{3}}$, the principal part of ψ is equal to the principal part of

$$-\kappa'_0{}^{-2}\Sigma\, 3^{-\frac{1}{3}}z_0^{\frac{1}{3}}(2n+1)\frac{\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})}{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})}(1-\mu^2)\frac{d\mathrm{P}_n}{d\mu},$$

where the summation is extended on both sides of $n+\tfrac{1}{2}=z_0$, the appropriate approximations for $z_0^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z_0)$ given by relation (3) being substituted. Since the values of n involved in the summation are all large the appropriate approximation for $\mathrm{P}_n(\mu)$ is given by[*]

$$\mathrm{P}_n(\mu)=\mathrm{J}_0\{(2n+1)\sin\tfrac{1}{2}\theta\},$$

whence

$$(1-\mu^2)\frac{d\mathrm{P}_n}{d\mu}=(n+\tfrac{1}{2})\sin\theta\cos\tfrac{1}{2}\theta\mathrm{J}_1\{(2n+1)\sin\tfrac{1}{2}\theta\},$$

and the series becomes

$$-3^{-\frac{1}{3}}\kappa z_0^{-\frac{1}{3}}\Sigma\,2(n+\tfrac{1}{2})^2\sin\theta\cos\tfrac{1}{2}\theta\mathrm{J}_1\{(2n+1)\sin\tfrac{1}{2}\theta\}\frac{\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})}{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})}$$

Now, to the order of approximation required,

$$\mathrm{J}_1\{(2n+1)\sin\tfrac{1}{2}\theta\}=\{2\pi(2n+1)\sin\tfrac{1}{2}\theta\}^{-\frac{1}{2}}\left[e^{(2n+1)\iota\sin\frac{1}{2}\theta-\frac{3}{4}\pi\iota}\right.$$
$$\left.+e^{-(2n+1)\iota\sin\frac{1}{2}\theta+\frac{3}{4}\pi\iota}\right],$$

and the series becomes

$$-2\cdot3^{-\frac{1}{3}}\pi^{-\frac{1}{2}}\kappa z_0^{-\frac{1}{3}}(\sin\tfrac{1}{2}\theta)^{\frac{1}{2}}\cos^2\tfrac{1}{2}\theta\Sigma(n+\tfrac{1}{2})^{\frac{3}{2}}\left[e^{(2n+1)\iota\sin\frac{1}{2}\theta-\frac{3}{4}\pi\iota}\right.$$
$$\left.+e^{-(2n+1)\iota\sin\frac{1}{2}\theta+\frac{3}{4}\pi\iota}\right]\frac{\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})}{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})}.$$

Again

$$n+\tfrac{1}{2}=z_0+3^{-\frac{1}{3}}\cdot 6^{-\frac{1}{3}}z_0^{\frac{1}{3}}\zeta,$$

therefore the principal part $\overline{\psi}$ of ψ is given by

$$\overline{\psi}=-2\pi^{-\frac{1}{2}}\kappa(3z_0)^{-\frac{1}{3}}(z_0^{\frac{1}{2}}\sin\tfrac{1}{2}\theta)^{\frac{1}{2}}\cos^2\tfrac{1}{2}\theta\left[e^{2\iota z_0\sin\frac{1}{2}\theta-\frac{3}{4}\pi\iota}\mathrm{S}_1+e^{-2\iota z_0\sin\frac{1}{2}\theta+\frac{3}{4}\pi\iota}\mathrm{S}_2\right].$$

where

$$\mathrm{S}_1=\Sigma e^{6^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta\iota\sin\frac{1}{2}\theta}\frac{\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})}{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})},\qquad \mathrm{S}_2=\Sigma e^{-6^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta\iota\sin\frac{1}{2}\theta}\frac{\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})}{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})},$$

The functions $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$, $\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})$ are integral functions of $\xi^{\frac{1}{3}}$, therefore $\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})/\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})$ can be expressed in the form

$$\sum_{\iota=0}^{\infty}\frac{A_k}{\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi\iota}},$$

where A_k is the value of

$$2\xi^{\frac{1}{3}}K_1(\xi e^{-\pi\iota})/3\xi^{\frac{1}{3}}\frac{\partial}{\partial\xi}\{\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi\iota})\},$$

when

$$\xi^{\frac{1}{3}}=x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi\iota},$$

[*] 'Lond. Math. Soc. Proc.,' vol. 31, p 269 (1899)

that is
$$A_k = 2x_k^{\frac{1}{2}}(3a_k)^{-1}e^{-\frac{1}{3}\pi i},$$

and
$$\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi i})/\xi^{\frac{1}{3}}K_{\frac{1}{3}}(\xi e^{-\pi i}) = 2\sum_{k=0}^{\infty}x_k^{\frac{1}{2}}(3x_k)^{-1}e^{-\frac{1}{3}\pi i}/(\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}),$$

hence
$$S_1 = 2\sum e^{\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}\sum_{k=0}^{\infty}x_k^{\frac{1}{2}}(3x_k)^{-1}e^{-\frac{1}{3}\pi i}/(\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}),$$

$$S_2 = 2\sum e^{-\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}\sum_{k=0}^{\infty}x_k^{\frac{1}{2}}(3x_k)^{-1}e^{-\frac{1}{3}\pi i}/(\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i})$$

The principal part of
$$\sum e^{\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}/(\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i})$$

is the integral
$$3 \; 6^{-\frac{1}{3}}z_0^{\frac{1}{3}}\int_{-\infty}^{\infty}\frac{e^{\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}}{\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}}\,d\zeta,$$

for
$$n+\tfrac{1}{2} = z_0+3 \; 6^{-\frac{1}{3}}z_0^{\frac{1}{3}}\zeta,$$

and since the exponential tends to zero at infinity in the upper half of the ζ plane, and the only singularity of the integrand at a finite distance, viz., $\zeta = 2^{-\frac{1}{3}}x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}$ is in the lower half of the ζ plane, this integral vanishes and therefore the principal part of S_1 vanishes. The principal part of
$$\sum e^{-\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}/(\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i})$$

is the integral
$$3 \; 6^{-\frac{1}{3}}z_0^{\frac{1}{3}}\int_{-\infty}^{\infty}\frac{e^{-\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}}{\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}}\,d\zeta,$$

and the exponential tends to zero at infinity in the lower half of the ζ plane, therefore this integral is equivalent to the integral
$$-3 \cdot 6^{-\frac{1}{3}}z_0^{\frac{1}{3}}\int_{(0)}\frac{e^{-\theta^{\frac{1}{3}}z_0^{\frac{1}{3}}\zeta_i \sin\frac{1}{3}\theta}}{\xi^{\frac{1}{3}}-x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}}\,d\zeta,$$

where the path of integration is any closed curve, which encloses the singularity of the integrand, that is $\zeta = 2^{-\frac{1}{3}}x_k^{\frac{1}{3}}e^{\frac{1}{3}\pi i}$, the value of this integral is
$$-3^{\frac{1}{3}}\pi i z_0^{\frac{1}{3}}e^{-2^{\frac{1}{3}}x_k^{\frac{1}{3}}z_0^{\frac{1}{3}}e^{\frac{1}{3}\pi i}\sin\frac{1}{3}\theta},$$

whence the principal part of S_2 is
$$-3^{-\frac{1}{3}}2\pi i z_0^{\frac{1}{3}}\sum_{k=0}e^{\frac{1}{3}\pi i}x_k^{-\frac{1}{2}}e^{-(3x_k)^{\frac{1}{3}}z_0^{\frac{1}{3}}\sin\frac{1}{3}\theta}\,e^{\frac{1}{3}\pi i},$$

and therefore the principal part of ψ is given by
$$\overline{\psi} = -4\pi^{\frac{1}{2}}\kappa\iota(z_0^{\frac{1}{3}}\sin\tfrac{1}{3}\theta)^{\frac{1}{2}}\cos^2\tfrac{1}{3}\theta \; e^{-2z_0\sin\frac{1}{3}\theta+i\frac{1}{3}\pi i}\sum_{k=0}^{\infty}(3x_k)^{-\frac{1}{2}}e^{-(3x_k)^{\frac{1}{3}}e^{\frac{1}{3}\pi i}z_0^{\frac{1}{3}}\sin\frac{1}{3}\theta},$$

If $\psi_1 e^{\iota \kappa \nabla t}$ is the value of $\gamma r \sin \theta$ due to the oscillator alone, the principal part of ψ_1 is

$$\overline{\psi}_1 = -\iota \kappa \cos^2 \tfrac{1}{2} \theta \, e^{-2\iota z_0 \sin \frac{1}{2}\theta},$$

hence

$$\overline{\psi} = 4\pi^{\frac{1}{2}} (z_0^{\frac{1}{2}} \sin \tfrac{1}{2}\theta)^{\frac{1}{2}} \overline{\psi}_1 e^{\iota \frac{1}{4}\pi \iota} \sum_{k=0}^{\infty} (3x_k)^{-\frac{1}{2}} e^{-(3x_k)^{\frac{1}{2}} (z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta) e^{\frac{1}{4}\pi \iota}} \quad (5)$$

When the point P is at a considerable distance from the oscillator the first term of this series will give a sufficient approximation, but, as the distance from the oscillator diminishes, a greater number of terms is required, and, when the distance is such that $z_0^{\frac{1}{2}} \sin \frac{1}{2} \theta$ is small, the series converges very slowly, ultimately tending to the form $\Sigma \{(k+\frac{1}{4})\pi\}^{-\frac{1}{2}}$, since from (4) x_k tends to $(k+\frac{1}{4})\pi$, when k is a large number, and this series diverges. The value to which $\overline{\psi}$ tends as θ tends to zero can be obtained as follows. The series

$$\sum_{k=0}^{\infty} (3x_k)^{-\frac{1}{2}} e^{-(3x_k)^{\frac{1}{2}} z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta e^{\frac{1}{4}\pi \iota}}$$

tends to the same value as the integral

$$\frac{1}{3\pi} \int_0^{\infty} e^{-u^{\frac{1}{2}} z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta e^{\frac{1}{4}\pi \iota}} u^{-\frac{2}{3}} du,$$

that is as the integral

$$\frac{1}{2\pi} \int_0^{\infty} e^{-v z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta e^{\frac{1}{4}\pi \iota}} v^{-\frac{1}{2}} dv,$$

which has the value $\frac{1}{2} \pi^{-\frac{1}{2}} (z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta)^{-\frac{1}{2}} e^{-\frac{1}{8}\pi \iota}$, and therefore, as θ tends to zero, $\overline{\psi}$ tends to the value $2\overline{\psi}_1$, the value to be expected.

The preceding analysis neglects the terms for which $|n+\frac{1}{2}-z_0|$ is of higher order than $z_0^{\frac{1}{3}}$, it will now be proved that the inclusion of these terms does not affect the result, for, when $n+\frac{1}{2}-z$ is of higher order than $z^{\frac{1}{3}}$ the approximate value of $z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z) \Big/ \dfrac{\partial}{\partial z} \{z^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota z)\}$ is $(\sinh \delta)^{-1}$, and when $z-n-\frac{1}{2}$ is of higher order than $z^{\frac{1}{3}}$ the approximate value is $-\iota \sec \alpha,$[*] that is in both cases $z \{(n+\frac{1}{2})^2 - z^2\}^{-\frac{1}{2}}$. Further $(z/3)^{\frac{1}{3}} \xi^{\frac{1}{2}} K_{\frac{1}{3}}(\xi e^{-\pi \iota}) / \xi^{\frac{1}{2}} K_{\frac{2}{3}}(\xi e^{-\pi \iota})$ approximates to the value $(z/3\xi)^{\frac{1}{2}}$, that is $z^{\frac{1}{3}} \{2(n+\frac{1}{2}-z)\}^{-\frac{1}{2}}$ for all values of ζ except those which lie in the neighbourhood of the line $e^{\frac{1}{3}\pi \iota}$. The series (2) now becomes

$$\psi = \sum_{1}^{n_1} \frac{z_0}{\{(n+\frac{1}{2})^2 - z_0^2\}^{\frac{1}{2}}} (1-\mu^2) \frac{dP_n}{d\mu} + \sum_{n_1}^{n_2} \left(\frac{z_0}{3}\right)^{\frac{1}{3}} \frac{\xi^{\frac{1}{2}} K_{\frac{1}{3}}(\xi e^{-\pi \iota})}{\xi^{\frac{1}{2}} K_{\frac{2}{3}}(\xi e^{-\pi \iota})} (1-\mu^2) \frac{dP_n}{d\mu}$$

$$+ \sum_{n_2}^{\infty} \frac{z_0}{\{(n+\frac{1}{2})^2 - z_0^2\}^{\frac{1}{2}}} (1-\mu^2) \frac{dP_n}{d\mu}.$$

* 'Phil. Trans.,' A, vol. 210

and it appears at once, when the summation is replaced by integration, that the inclusion of these terms has not altered the singularities, hence the result is not altered

The values of the amplitude of the ratio $\bar{\psi}/\bar{\psi}_1$, which is the same thing as the value of the amplitude of the ratio of the electric force at the surface to the electric force in the same direction due to the oscillator alone, have been calculated from the formula for values of θ from 6° upwards at intervals of 20' of arc, in the calculation the first term of the series has alone been taken, the effect of the second term is negligible except for the first three entries in the last column and the first entry in the preceding column, when the second place of decimals is possibly affected. The wave-lengths are those that correspond to the values 50, 40, 32, 25, 20 of $(\kappa a)^{\frac{1}{4}}$, that is, for the earth's surface wave-lengths of 320, 625, 1220, 2560, 5000 metres, the distance d in miles is given in the second column

θ	Miles	$\lambda =$ 320 metres	$\lambda =$ 625 metres	$\lambda =$ 1220 metres	$\lambda =$ 2560 metres	$\lambda =$ 5000 metres
6 0	419	0 18	0 34	0 54	0 80	1 04
6 20	442	0 15	0 30	0 49	0 74	0 96
6 40	465	0 13	0 26	0 44	0 69	0 98
7 0	489	0 11	0 22	0 40	0 64	0 88
7 20	512	0 09	0 19	0 36	0 59	0 88
7 40	535	0 07	0 17	0 32	0 55	0 78
8 0	559		0 15	0 29	0 50	0 73
8 20	582		0 13	0 26	0 46	0 69
8 40	605		0 11	0 23	0 43	0 65
9 0	628		0 09	0 21	0 39	0 61
9 20	652		0 08	0 18	0 36	0 57
9 40	675		0 07	0 16	0 33	0 53
10 0	698			0 14	0 30	0 50
10 20	721			0 13	0 28	0 47
10 40	745			0 11	0 26	0 44
11 0	768			0 10	0 24	0 41
11 20	791			0 09	0 22	0 38
11 40	814			0 08	0 20	0 36
12 0	837				0 18	0 34
12 20	861				0 16	0 32
12 40	884				0 15	0 30
13 0	907				0 14	0 28
13 20	931				0 13	0 26
13 40	954				0 12	0 24
14 0	977				0 11	0 22
14 20	1000				0 10	0 21
14 40	1024				0 09	0 20
15 0	1047				0 08	0 18
15 20	1070				0 08	0 17
15 40	1094					0 16
16 0	1117					0 15
16 20	1140					0 14
16 40	1164					0 13
17 0	1187					0 12
17 20	1210					0 11
17 40	1233					0 10
18 0	1257					0 10

To find the absolute value of the ratio of the electric forces at two different distances it has to be observed that if θ and θ' are these distances, E and E' the electric forces at them, then the ratio of the two numbers in the table corresponding to θ and θ' is the ratio $E \sin \frac{1}{2}\theta / E' \sin \frac{1}{2}\theta'$, for example, for a wave-length of 5000 metres, the ratio E/E' for distances of 600 and 1200 miles is very approximately $1/12$

The effect of the distance of the oscillator from the surface, when this distance is very small compared with the radius of the sphere, can be obtained from the series (2) For, $z_1 - z_0$ being very small compared with z_0,

$$z_1^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z)$$
$$= z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) + (z_1 - z_0) \frac{\partial}{\partial z_0} \{ z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) \} + \frac{1}{2} (z_1 - z_0)^2 \frac{\partial^2}{\partial z^2} \{ z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) \},$$

neglecting higher powers of $z_1 - z_0$ than $(z_1 - z_0)^2$, that is

$$z_1^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z) = z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) + 2 z_1 \sin^2 \frac{1}{2} \epsilon_1 \frac{\partial}{\partial z_0} \{ z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0) \}$$
$$+ 2 \cdot 6^{\frac{1}{2}} z_0^{-1} z_1^2 \sin^4 \frac{1}{2} \epsilon_1 \zeta z_0^{\frac{1}{2}} K_{n+\frac{1}{2}} (\iota z_0),$$

where ϵ_1 is the angular distance of the line of contact of the geometrical shadow with the sphere from the oscillator, and, therefore, the principal part of ψ is equal to the principal part of

$$-3^{-\frac{1}{2}} \kappa z_1^{-2} z_0^{\frac{1}{2}} \Sigma (2n+1) \left[\frac{\xi^{\frac{1}{2}} K_1 (\xi e^{-\pi\iota})}{\xi^{\frac{1}{2}} K_{\frac{1}{2}} (\xi e^{-\pi\iota})} \{ 1 + 2 \cdot 6^{\frac{1}{2}} z_0^{-1} z_1^2 \zeta \sin^4 \frac{1}{2} \epsilon_1 \} \right] (1 - \mu^2) \frac{\partial P_n}{\partial \mu}$$

From this, by the previous analysis, it follows that

$$\overline{\psi} = -4 \pi^{\frac{1}{2}} \iota \kappa z_0^2 z_1^{-3} \{ z_0^{\frac{1}{2}} \sin \frac{1}{2} \theta \}^{\frac{1}{2}} \cos^2 \frac{1}{2} \theta e^{-2\iota z_0 \sin \frac{1}{2}\theta + \frac{1}{4}\pi\iota} \sum_{k=0}^{\infty} [(3 x_k)^{-1}$$
$$+ 2 e^{\frac{1}{4}\pi\iota} z_0^{-\frac{1}{2}} z_1^2 \sin^4 \frac{1}{2} \epsilon_1] e^{-(3x_k)^{\frac{1}{2}} (z_0^{\frac{1}{2}}\sin\frac{1}{2}\theta) e^{\frac{1}{4}\pi\iota}}$$

In this case

$$\overline{\psi}_1 = -\iota\kappa \cos^2 \frac{1}{2}\theta \, e^{-2\iota z_0 \sin \frac{1}{2}\theta} [1 - 2\iota z_1 \sin^2 \frac{1}{2} \epsilon_1 \sin \frac{1}{2}\theta + \iota z_1 \sin^4 \frac{1}{2} \epsilon_1 \cos^2 \frac{1}{2}\theta \, \mathrm{cosec} \frac{1}{2}\theta],$$

and, to the order required

$$\psi = 4\pi^{\frac{1}{2}} \{ z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta \}^{\frac{1}{2}} e^{\frac{1}{4}\pi\iota} \overline{\psi}_1 [(1 + 2 \iota z_0 \sin^2 \frac{1}{2} \epsilon_1 \sin \frac{1}{2}\theta$$
$$+ \iota z_0 \sin^4 \frac{1}{2} \epsilon_1 \cos^2 \frac{1}{2}\theta \, \mathrm{cosec} \frac{1}{2}\theta) F_1 + 2 (z_0^{\frac{1}{2}} e^{\frac{1}{4}\pi\iota} \sin^4 \frac{1}{2} \epsilon_1) F_2],$$

where

$$F_1 = \sum_{k=0}^{\infty} (3 x_k)^{-\frac{1}{2}} e^{-(3x_k)^{\frac{1}{2}} (z_0^{\frac{1}{2}}\sin\frac{1}{2}\theta) e^{\frac{1}{4}\pi\iota}}, \qquad F_2 = \sum_{k=0}^{\infty} e^{-(3x_k)^{\frac{1}{2}} (z_0^{\frac{1}{2}}\sin\frac{1}{2}\theta) e^{\frac{1}{4}\pi\iota}}$$

As θ diminishes and becomes very small, the series F_2 converges more slowly than F_1, but as θ tends towards ϵ_1, F_2 tends towards the same value as the integral

$$\frac{1}{2\pi} \int_0^\infty e^{-y (z_0^{\frac{1}{2}} \sin \frac{1}{2}\theta) e^{\frac{1}{4}\pi\iota}} y^{\frac{1}{2}} dy,$$

which has the value

$$\tfrac{1}{4}\pi^{-\frac{1}{2}}\,(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\theta)^{-1}\,e^{-\frac{1}{4}\pi i},$$

and therefore as θ tends to ϵ_1, $\overline{\psi}$ tends to the value

$$2\,\overline{\psi}_1\,(1+2\,\iota z_0\sin^3\tfrac{1}{2}\,\epsilon_1+\iota z_0\sin^3\tfrac{1}{2}\,\epsilon_1\cos^2\tfrac{1}{2}\,\epsilon-\iota z_0\sin^3\tfrac{1}{2}\,\epsilon_1),$$

that is to the value $\qquad 2\,\overline{\psi}_1\,(1+2\iota z_0\sin^3\tfrac{1}{2}\,\epsilon_1),$

which is finite. When the point P on the surface is at a distance from the oscillator for which the first term in each series is alone significant, the ratio of the amplitude of the term due to the height of the oscillator above the surface to the term independent of the height is $2(3z_0)^{\frac{1}{3}}(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\epsilon_1)^4$, that is $3\,234(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\epsilon_1)^4$

For a height of 500 feet and a wave-length corresponding to $z_0^{\frac{1}{3}}=50$ the value of this ratio is approximately 0 003

The result can also be obtained when the point P and the oscillator are both at very small distances from the surface   For, writing

$$z^{\frac{1}{3}}J_{n+\frac{1}{2}}(z_0)\frac{\partial}{\partial z_0}\{z_0 K_{n+\frac{1}{2}}(\iota z_0)\}-z_0^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z_0)\frac{\partial}{\partial z_0}\{z_0^{\frac{1}{3}}J_{n+\frac{1}{2}}(z_0)\}=\mathrm{G},$$

it follows that

$$z^{\frac{1}{3}}J_{n+\frac{1}{2}}(z)\frac{\partial}{\partial z_0}\{z_0 K_{n+\frac{1}{2}}(\iota z_0)\}-z^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z)\frac{\partial}{\partial z_0}\{z_0 J_{n+\frac{1}{2}}(z_0)\}$$
$$=\mathrm{G}+\tfrac{1}{2}(z-z_0)^2\{n(n+1)/z_0^2-1\}\,\mathrm{G},$$

that is

$$z^{\frac{1}{3}}J_{n+\frac{1}{2}}(z)\frac{\partial}{\partial z_0}\{z_0 K_{n+\frac{1}{2}}(\iota z_0)\}-z^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z)\frac{\partial}{\partial z_0}\{z_0 J_{n+\frac{1}{2}}(z_0)\}$$
$$=-[1+2\;6^{\frac{1}{3}}(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\epsilon)^4\zeta]\,e^{-\frac{1}{3}(n+\frac{1}{2})\pi i},$$

where ϵ is the angular distance of the line of contact of the tangent cone from the point P to the surface from the point P, and, therefore, to the same order as in the former case,

$$\psi=-\kappa z_0^{-2}\Sigma(2n+1)\{1+2\;6^{\frac{1}{3}}(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\epsilon)^4\,\zeta+2.6^{\frac{1}{3}}(z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\epsilon_1)\,\zeta\}$$
$$\times\frac{z_0^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z_0)}{\dfrac{\partial}{\partial z_0}\{z_0^{\frac{1}{3}}K_{n+\frac{1}{2}}(\iota z_0)\}}(1-\mu^2)\frac{\partial P_n}{\partial \mu}.$$

From the previous analysis it immediately follows that

$$\overline{\psi}=-4\pi^{\frac{1}{3}}\iota\kappa\cos^2\tfrac{1}{2}\theta\,\{z_0^{\frac{1}{3}}\sin\tfrac{1}{2}\theta\}^{\frac{1}{3}}\,e^{-2\iota z_0\sin\frac{1}{3}\theta+\frac{1}{4}\pi i}$$
$$\times\sum_{k=0}^{\infty}[(3a_k)^{-\frac{1}{3}}+2z_0^{\frac{1}{3}}(\sin^4\tfrac{1}{2}\epsilon+\sin^4\tfrac{1}{2}\epsilon_1)\,e^{\frac{1}{3}\pi i}]\,e^{-(3z_0)^{\frac{1}{3}}[z_0^{\frac{1}{3}}\sin\frac{1}{3}\theta]\,a_k\pi i},$$

that is

$$\bar{\Psi} = -4\pi^{\frac{1}{2}} \iota \kappa \cos^2 \tfrac{1}{2}\theta \, \{z_0^{\frac{1}{2}} \sin \tfrac{1}{2}\theta\}^{\frac{1}{2}} \, e^{2\iota z_0 \sin \frac{1}{2}\theta + \iota\gamma m}$$

$$\times [F_1 + 2z_0^{\frac{1}{2}} (\sin^4 \tfrac{1}{2}\epsilon + \sin^4 \tfrac{1}{2}\epsilon_1) e^{\frac{1}{2}\pi\iota} F_y]$$

The corresponding results for a perfectly absorbing surface or an imperfectly conducting surface can be obtained from the above [*]

The Electrical Condition of a Gold Surface during the Absorption of Gases and their Catalytic Combustion

By Harold Hartley, M Sc [†]

Introduction

In 1905 Bone and Wheeler, in their memoir upon "The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces,"[‡] drew attention to the possible connection between the electrical conditions of hot surfaces and their power of rendering "condensed" or "occluded" gases chemically active Shortly afterwards Bone and Makower, in a series of unpublished experiments, observed that a gold surface becomes negatively electrified during the catalytic combination of hydrogen and oxygen at 300° or thereabouts

The recent inventions, by Bone and his co-workers, of processes of "flameless incandescent surface combustion," whereby the constituents of an explosive gaseous mixture, in correct combining proportions, are caused to combine at a highly accelerated rate, and without development of flame, in contact with (or within the pores or interstices of) an incandescent solid, have again called attention to the important *rôle* played by hot surfaces in accelerating combustion, and to the great economic advantages derivable therefrom. The phenomenon is now known to depend upon a peculiar "activation" of the combustible gas, and probably of the oxygen also, by

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association with the surface   At relatively low temperatures the intensity of such action varies with the chemical characters and physical condition of the surface, but it rapidly increases with the temperature until at bright incandescence there is little to choose between the catalysing power of chemically different surfaces, porosity and refractoriness being now the dominant factors [*]

In a discussion upon the subject at the British Association in 1910, Sir J J Thomson remarked, "It was not improbable that the emission of charged particles from the surface was a factor of primary importance   " and he suggested "that the action of surfaces might ultimately be found to depend on the fact that they formed a support for layers of electrified gas in which chemical charges proceed with high velocity "[†]

The experiments recorded in this paper were carried out by the author under the supervision of Prof Bone, while holding the Research Fellowship established by the Institution of Gas Engineers at the University of Leeds, they prove the existence of an intimate relationship between the occlusion of gas by a hot metallic surface and its electrical condition, whilst indirectly they lend support to the view, recently put forward by J A Harker,[‡] J N Pring,[§] and others, that the well known electronic emission from incandescent solids is probably dependent upon the occlusion of gas

Experimental

The Apparatus—Gold was selected as the most suitable metal for the principal experiments because (1) of its marked catalysing power at moderate temperatures, and (2) of its not forming any definite chemical compound with any of the gases under investigation (hydrogen, carbon monoxide, or oxygen)   For whilst it is not nearly so active in promoting combustion at low temperatures as metals of the platinum group, its action is more amenable to control than theirs, moreover, although its activity is of about the same order as that of nickel, it displays no appreciable tendency to either oxide or carbonyl formation under the required experimental conditions

The metal was employed in the form of a gauze of fine gold wire, of 22 strands (each 0 15 mm in diameter) per centimetre, which had been specially woven by Messrs Johnson and Matthey for Bone and Wheeler's experiments (*loc cit.*)

* Bone, 'Journ Franklin Institute,' 1912, p 107 ; also 'Ber Deut Chem. Ges.,' 1913, vol 46, p. 14

† 'Brit Assoc Reports,' 1910 (Sheffield), p. 501

‡ J A Harker and G W C Kaye, 'Roy Soc Proc.,' A, vol 86, p 379 (1912), and A, vol 88, p. 522 (1913)

§ J N Pring, 'Roy Soc. Proc.,' A, vol. 89, p. 344 (1913).

An insulated roll, A (see diagram), of this gauze was suspended from a gold wire, A′A′, in a cylindrical Jena-glass bulb, BB, of about 75 c.c capacity, which was heated to the desired experimental temperature in the air-bath, DD, the gas supply of which was suitably controlled   The gold wire, A′A′, was threaded through the horizontal glass capillary tube C, which passed through the ebonite plug F.   The joints between (1) wire and glass at O, (2) the tube C and plug F, and (3) the plug F and the lateral branch, EE, of the main apparatus, were rendered air-tight by means of sealing wax; the gauze A thus insulated was connected through the wire A′A′A′ with a quadrant electrometer (not shown in the diagram)
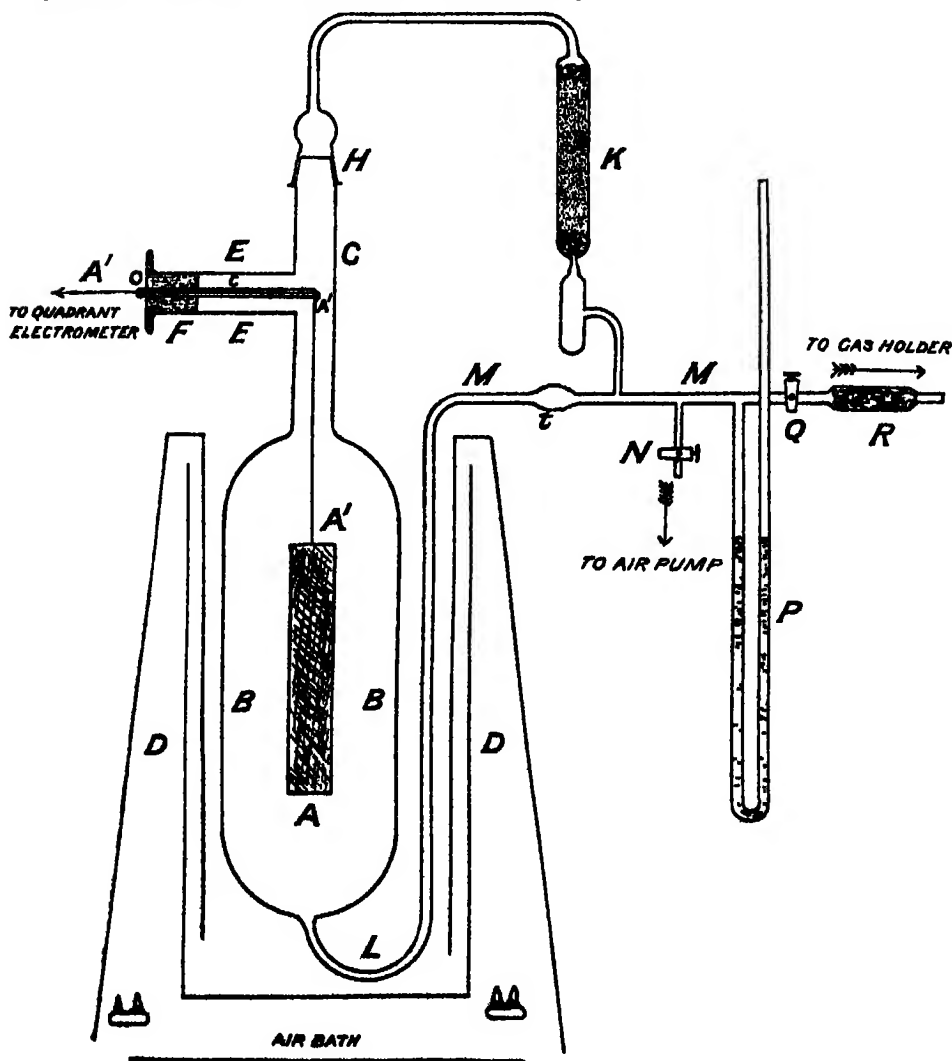
As to the remaining parts of the apparatus, the upper part of the bulb BB terminated in a wide vertical tube G, leading through a ground-glass joint, H, to a tube, K, containing phosphoric anhydride, previously re-distilled in a current of dry oxygen over platinised asbestos   The under part of A terminated in a narrow hard-glass tube L, which was bent round, first into a vertical direction and then (after its projection out of the air-bath) into the horizontal branch MM, as shown in the diagram   Lateral branches from MM served (1) to complete the circuit (through K) with the head of the apparatus, (2) for the evacuation of the apparatus through the stopcock N, and (3) for connection with the mercurial pressure gauge P   The gas under examination entered the apparatus through the stopcock Q, having previously traversed a tube R packed with glass-wool.

The difference in temperature between the bulb A and the upper part of the apparatus was sufficient to maintain a slow movement of the gas in the apparatus during an experiment, whilst the phosphoric anhydride in K kept it dry   The whole of the apparatus was protected from external electrostatic effects by sheathing it in aluminium foil, which was " earthed "

1st Series —*Proof of Negative Charge during the Combination of Hydrogen and Oxygen in Contact with the Surface*

These experiments confirmed the previous observation of Bone and Makower, the apparatus was exhausted and the temperature of the bulb A raised to a degree (about 350°) sufficient to make the gauze active towards electrolytic gas *   The electrometer was thereupon " earthed," and electrolytic gas (prepared by the electrolysis of a solution of barium hydroxide) was slowly admitted into the apparatus up to a pressure of 450 mm or thereabouts   As soon as the combination of the gases in contact with the gauze had begun, the earth connection with the electrometer was broken   There was always a steady movement of the spot of light along the scale up to about 55 divisions (sensibility = 235 divisions per volt) in a negative direction, corresponding to a negative charge of approximately 0 2 volt on the gauze   Such a result could be repeated indefinitely, and the question arose. Is it to be ascribed to the actual chemical combination of the two gases at the surface, or to the absorption of the gases by the metal which presumably precedes this combination ?   It was therefore necessary to study the effects produced when each gas is separately absorbed by the metal

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* The temperature indicated by the thermometer of the air-bath was doubtless higher than that of the gauze itself, Bone and Wheeler (*loc. cit.*) found that a temperature of 250° sufficed to make the gauze active towards electrolytic gas.

2nd Series — *The Electrical Effect due to Absorption of Hydrogen*

At the conclusion of the previous series, the apparatus was evacuated for three hours, and the temperature of the air-bath raised to 478° Carefully purified hydrogen was thereupon introduced up to a pressure of 715 mm, and after a further interval of $2\frac{1}{2}$ hours the electrical condition of the gauze was examined, it was then found to have acquired a negative charge of approximately 1-2 volt The temperature of the enclosure was thereupon lowered to 370° and, on the following day (the gas having remained in contact with the metal overnight), the following series of observations were made, indicating a rapid charging up of the gauze after successive "earthings" The sensibility of the electrometer (charge on needle = 200 volts) was 147 scale divisions for a charge of one volt

Observation	Hour	Temperature of enclosure	Electrometer reading Scale divisions
(1)	10 46 10 46½ Electrometer earthed	362°	0 −244
(2)	10 50 10 50½ Electrometer earthed	367°	0 −172
(3)	10 52 10 52½ Electrometer earthed	370°	0 −182
(4)	10 55 10 55½ Electrometer earthed	370°	0 −176
(5)	10 57 10 57½ Electrometer earthed	373°	0 −176

Observations (2) to (5) inclusive showed the gauze between each successive insulation and "earthing" acquired a negative charge of approximately 1-2 volts in 15 secs.

The sensibility of the electrometer was then reduced to 120 scale divisions per volt (charge on needle = 80 volts), and the experiment continued The gauze now charged up, at a rate of about 1·1 volt per minute, to a steady maximum of −1 5 volt

3rd Series — *On the Electrical Effects due to the Absorption of Oxygen*

Immediately after the conclusion of the previous series, the apparatus was exhausted, the temperature of the bath being meanwhile maintained at 370

to 390°   On admitting oxygen, the gauze continued to show a negative charge, which gradually diminished in intensity, however, during a period of several days, and finally gave place to a steady positive charge of + 0 8 volt, which subsequent experiments proved to be the true oxygen effect

This greatly delayed manifestation of the true oxygen effect is doubtless to be ascribed to the masking effect of hydrogen occluded during the previous series of experiments, which was obstinately retained by the metal, long after the substitution of oxygen for hydrogen in the surrounding atmosphere

Indeed, the evidence of the research as a whole pointed to two important conclusions, namely (1) that an occluded gas can only be removed with great difficulty by mere exhaustion, and will continue to manifest its peculiar effect on the electrical condition of the metal for a considerable time, even when another gas with an opposite effect is being absorbed, so that the true effect of the latter may be for a time masked, and (2) that the charge acquired by the metal is due to gas leaving (not entering) it, after deep occlusion, a circumstance of considerable interest in connection with the phenomenon of surface combustion

4th Series —*On the Electrical Effects due to the Absorption of Carbon Monoxide*

After the conclusion of the previous series the gauze was kept at the room temperature for a month in contact with air   The apparatus was then heated up to 350°, and after a full day's exhaustion at that temperature pure dry carbonic oxide was admitted up to a pressure of 463 mm   For some days the gauze continued to show a positive charge, owing to the masking effect of the residual occluded oxygen from the previous series of experiments.   This positive charge, as well as the rate of charging up after successive "earthings" of the metal, gradually diminished, until finally (the temperature of the apparatus having meanwhile been raised to 400°) the true negative effect of the carbon monoxide, which in two successive experiments amounted to about —0 5 volt, asserted itself

On subsequently lowering the temperature rather rapidly from 400° to 350°, and again testing, the gauze showed for some minutes practically no charge at all, but shortly afterwards again developed a strong negative charge   On further rapidly lowering the temperature to about 300° the same thing was again observed, namely, a temporary absence of electrical effect, followed a few minutes later by a strong negative charge, this time of —1·0 volt.   Finally, on rapidly lowering the temperature to 250°, the effect again temporarily disappeared.

The above facts would seem to indicate that the electrical effect is really

due to occluded gas leaving the metal, for on rapidly lowering the temperature the outward flow of gas would be temporarily checked or lessened, producing a cessation or lag in the electrical effect, which was always a marked feature in the experiments

In further support of this view may be cited some later observations on the effects of successive sudden reduction in pressure upon the magnitude of the negative charge on an insulated silver rod maintained at a constant temperature of 85° in an atmosphere of pure dry carbon monoxide, the effect of a sudden reduction in pressure would be to temporarily increase the outward flow of occluded gas from the metal, which, according to the above rise, should be accompanied by an increase in the intensity of the negative charge

A rod of pure silver, 3 mm in diameter (flattened at one end to 5 mm.), was fitted in a Jena glass tube by means of an ebonite plug, through which it was connected with the leaf of a Wilson tilted electroscope   The capacity of the apparatus was purposely made as small as possible so as to permit of a rapid lowering of pressure in the gaseous atmosphere surrounding the rod   The actual observations were made after the rod had been maintained in contact with carbon monoxide at atmospheric pressure for a week at a temperature of 90–95° for most of the time, during which it had consistently shown a marked negative charge   The temperature was finally adjusted at 85°, and starting with a pressure (P_{oo}) of 754 mm the effect of successive rapid diminutions in pressure upon the negative potential rod were recorded, as under :—

	(1)	(2)	(3)	(5)
Temperature	85°	85°	85°	87°
P_{oo}	754	389	196 5	106 5
Deviation of the electroscope leaf	36	55	61 ·0	72 0
Deviation for a charge of −2/3 volt on electroscope leaf	68	70	70 0	76 0

The marked rise in the negative potential of the rod after each successive reduction in the pressure of the carbon monoxide atmosphere clearly indicated that the electrical effect is due to occluded gas leaving the metal

5th Series —*Experiments on the Combination of* $2CO + O_2$ *over Gold*

To complete the investigation it only remained to carry out a series of observations upon the effect of the combination of a mixture of carbon monoxide and oxygen, in their combining proportions, in contact with the gold gauze similar to those already made (1st Series) in the case of electrolytic

gas. For this purpose a U-tube containing solid caustic potash, as well as a long glass spiral immersed in liquid air, were sealed in series into the upper part of the apparatus outside the air-bath to remove any carbon dioxide formed, as rapidly as possible the temperature of the air-bath was raised to 370°, and after prolonged exhaustion at that temperature the mixture of carbon monoxide and oxygen in their combining ratios was admitted The gauze now rapidly developed a negative charge of −0 7 to −0 85 volt, which was repeatedly re-established within about one minute after each of many successive momentary "earthings" of the metal

Conclusion

The results of the investigation may be summarised in the following conclusion :—

(1) A gold surface acquires a negative charge during the catalytic combustion of gases in contact with it

(2) This electrical effect is probably antecedent to the actual combustion, and is primarily due to " occlusion " phenomena

(3) The metal becomes negatively charged during the occlusion of the combustible gas (hydrogen or carbon monoxide), and positively charged during the occlusion of oxygen

(4) Such electrical effects are probably due to occluded gas which is leaving (rather than entering) the metal Any cause, such as a sudden lowering of temperature, which would momentarily check the outflow of occluded gas, will likewise diminish the intensity of the charge, or may even momentarily stop it altogether Conversely, a sudden diminution in the outside gaseous pressure in the vicinity of the metal, which would increase the rate of outflow of the occluded gas from the metal, will temporarily increase the intensity of the electrical effect.

(5) Such temporary disturbances in the intensities of the electrical effects as are described in (4) are probably due to the fact that a change in either temperature or pressure of the system is accompanied by a change in the dynamic equilibrium between the in-going and out-flowing gas at the surface system, which change lies behind the exciting cause

The bearing of the above conclusions upon the question of surface combustion will be discussed in a subsequent memoir embodying the results of further experiments by Prof. Bone and his pupils, who are now engaged upon extending the subject in the new Department of Chemical Technology at the Imperial College of Science and Technology, London

The Diffusion of Electrons through a Slit.

By J H MACKIE.

In a paper on " The Motion of Electrons in Gases," by Prof Townsend and Mr. Tizard* it was shown how, by measuring the lateral diffusion of a stream of electrons in an electric field, it is possible to find k, the factor by which the energy of agitation of the electrons exceeds that of the surrounding molecules   The ions come at a uniform rate through a slit S of width $2a$ in a large metal plate A, and traverse a distance r in the direction of an electric force Z   The plane of the plate A may be taken as that of xy, the origin of co-ordinates being the centre of the slit which latter is taken parallel to the axis of y The ions are received on three insulated electrodes, c_1, c_2, c_3, which were portions of a disc of diameter 7 cm., c_2 being a narrow strip 5 mm wide, cut from the centre of the disc and insulated by narrow air gaps from the two electrodes, c_1, c_3, on each side of it   The electric field between A and the electrodes C was maintained constant by a series of rings of diameter 7 cm , kept at uniformly decreasing potentials   In this case the differential equation giving the distribution n of electrons in the electric field is

$$\nabla^2 n = 41 \frac{Z}{k} \frac{\partial n}{\partial z}$$

If q is defined to be $\int n\,dy$, this equation becomes

$$\frac{\partial^2 q}{\partial x^2} + \frac{\partial^2 q}{\partial z^2} = 41 \frac{Z}{k} \frac{\partial q}{\partial z}$$

If n_1, n_2, n_3 are the charges received by the electrodes c_1, c_2, c_3, it is shown that the values of Z/k can be found by determining the ratio $R = n_2/(n_1 + n_2 + n_3)$, i.e the value of k corresponding to any Z can be found Experiments had previously been performed in which a circular stream of ions was collected on concentric circular electrodes, and from the results it appeared that the term $\partial^2 n/\partial x^2$ was small compared with the others   By neglecting this term, Prof Townsend obtained a solution of the differential equation in a simple form and plotted a curve with co-ordinates R and Z/k

It is desirable to know exactly what degree of accuracy is obtained by the simple method, and calculations of the values of R were made from the series which represents the solutions when the term $\partial^2 n/\partial x^2$ is retained

* 'Roy. Soc Proc,' A, vol 88 (1913)

The complete solution corresponding to the cylindrical boundary $r = 3\,5$ cm which was used in the experiments would be very complicated, but, as the width of the field was so large, very few ions travel outside the electrodes, and it will be quite allowable to assume the boundary to be rectangular, the width estimated parallel to x being 6 cm   For similar reasons the electrodes may be assumed to be portions of a rectangular plate of width 6 cm.   The number of ions in a strip of width dx will be $dx\int n\,dy$ or $q\,dx$

The problem, therefore, is to determine the charges acquired by the electrodes when the distribution q satisfies the differential equation

$$\frac{\partial^2 q}{\partial x^2} + \frac{\partial^2 q}{\partial z^2} = 41\frac{Z}{k}\cdot\frac{\partial q}{\partial z}$$

and the boundary conditions—

(i) at the upper plate, where $z = 0$,

$$q = q_0, \text{ when } x > -a \quad \text{and} \quad < a,$$

$$q = 0, \text{ when } x < -a \quad \text{and when} \quad x > a,$$

(ii) $q = 0$, when $x = \pm b$ for all values of z

$2b$ being the width of the boundary, or 6 cm,

$2a$ „   „   slit, or 0 2 cm

A solution of the differential equation is

$$q = \Sigma A e^{-\alpha z} \cos \mu x,$$

where, if 2λ be written for $41\,Z/k$,

$$\alpha = \sqrt{(\lambda^2 + \mu^2)} - \lambda$$

To satisfy the condition (ii),

$$\mu = \frac{(2s+1)\pi}{2b} \qquad (s = 0, 1, 2, 3, \quad)$$

Using the results

$$\int_{-b}^{b} \cos\frac{(2r+1)\pi x}{2b}\cos\frac{(2s+1)\pi x}{2b}\,dx = 0, \quad r \neq s,$$

$$= b, \quad r = s,$$

we find the coefficients of the Fourier expansion to be

$$A_s = \frac{4q_0}{\pi}\cdot\frac{1}{(2s+1)}\sin\frac{(2s+1)\pi a}{2b},$$

therefore $q = \dfrac{4q_0}{\pi}\Sigma e^{-\alpha z}\dfrac{1}{2s+1}\sin\dfrac{(2s+1)\pi a}{2b}\cos\dfrac{(2s+1)\pi x}{2b}$

The rate at which a charge is acquired by a strip dx of an electrode will be

$$dx \int nw\, dy = \theta\, dx \text{ (say)},$$

where w is the velocity in the direction of z of an electron moving under an electric force Z, w is given therefore by

$$\frac{nw}{K} = -\frac{\partial n}{\partial z} + 2\lambda n,$$

where K is the coefficient of diffusion

Therefore $\theta\, dx$ is proportional to

$$\left\{ \int \left(n - \frac{1}{2\lambda}\frac{\partial n}{\partial z} \right) dy \right\} dx, \quad \text{or} \quad \theta\, dx \propto dx \left(q - \frac{1}{2\lambda}\cdot\frac{\partial q}{\partial z} \right),$$

where q is evaluated at the electrode, $z = 4$

In the case of real electrodes, the presence of the metal would cause a slight change in the distribution at neighbouring points, but θ would be the charge received per unit time by a strip dx of a real electrode placed at a very small distance below the point at which θ is evaluated

From the expression already found for q we have

$$\theta \propto \frac{4q_0}{\pi} \Sigma \left(1+\frac{a}{2\lambda}\right) e^{-az} \frac{1}{2s+1} \sin\frac{(2s+1)\pi a}{2b}\sin\frac{(2s+1)\pi z}{2b}$$

If $2x_1$ is the width of electrode c_2,

$$n_2 = \int_{-x_1}^{x_1} \theta\, dx \propto \Sigma\left(1+\frac{a}{2\lambda}\right) e^{-ac} \frac{1}{(2s+1)^2} \sin\frac{(2s+1)\pi a}{2b}\sin\frac{(2s+1)\pi x_1}{2b},$$

therefore

$$R = \frac{n_2}{n_1+n_2+n_3}$$

$$= \frac{\Sigma \left(1+\frac{a}{2\lambda}\right) e^{-ac} \frac{1}{(2s+1)^2}\sin\frac{(2s+1)\pi a}{2b}\sin\frac{(2s+1)\pi r_1}{2b}}{\Sigma (-1)^s \left(1+\frac{a}{2\lambda}\right) e^{-ac} \frac{1}{(2s+1)^2}\sin\frac{(2s+1)\pi a}{2b}},$$

where $2\lambda = 41Z/k$ and $a = \sqrt{\left(\lambda^2 + (2s+1)^2\frac{\pi^2}{4b^2}\right)} - \lambda$

$$a = 0\,1 \text{ cm} \qquad b = 3 \text{ cm} \qquad c = 4 \text{ cm} \qquad x_1 = 0\,25 \text{ cm}$$

The following table gives the values of n_2, $n_1+n_2+n_3$ corresponding to different values of Z/k, the ratio of the charges $R = n_2/(n_1+n_2+n_3)$ is given in the fourth column of figures. The total number of ions coming through the slit is $0\,2 \times 2\lambda q_0 K$ (where K is the coefficient of diffusion), and the difference between the numbers in the third column and $0\,2$ represents

the number of ions that diffuse outwards and become discharged by the boundary at the distance of 3 cm from the central plane.

It will be seen that more than 99 per cent. of the ions that enter the field are collected by the electrodes when the ratio R exceeds 0 2

The fifth column contains the values of the ratio R' derived from the simplified equation

The values R' are those used by Prof Townsend and Mr. Tizard to deduce the values of k from the experimental determination of $n_2/(n_1 + n_2 + n_3)$

The agreement between the numbers in the fourth and fifth columns shows that the error introduced by neglecting the term $\partial^2 n/\partial x^2$ in the differential equation for n is negligible for the larger values of R, and rises to a 4-per-cent error when R is equal to 0 2 :—

Z/k	$n_2 + 2\lambda q_0 K$	$(n_1 + n_2 + n_3) + 2\lambda q_0 K$	R	R'
0	—	—	0 1851	—
0 1	0 031490	0 18923	0 1664	—
0 2	0 041373	0 19677	0 2082	0 200
0 5	0 062734	0 19988	0 3139	0 310
1 0	0 084980	0 19988	0 4248	0 425
1 5	0 101820	0 19990	0 5090	0 505
2 0	0 114040	0 20000	0 5701	0 570

Studies of the Processes Operative in Solutions. XXXI.—Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents—a Discussion of the Constitution of Sulphuric and other Polybasic Acids and of the Nature of Acids.

By Henry E. Armstrong (F.R S) and F. P Worley (D.Sc.), Professor of Chemistry in Auckland University College, New Zealand

"Most of the phlogistian chemists admit of the existence of vital air as a component part of acids, a position which seems indeed to be as well established upon fact as any part of the science of chemistry" 'The First Principles of Chemistry' By William Nicholson, London, 1790

Those who are conversant with the history of the development of our present theory of structure are aware that the constitution of lactic acid was the subject of discussion, in the years 1858–1860, by the distinguished German chemist Kolbe and the equally distinguished French chemist Wurtz, the latter contending that the acid was dibasic, whilst Kolbe held that it was a monatomic monobasic acid, viz hydroxypropionic acid—a view which has long been accepted.

The discussion has an important place in chemical literature, as it practically involved the recognition of the doctrine that organic acids owe their distinctive properties to the presence of the carboxyl radicle, (CO OH).

We propose to deal with sulphuric acid in a similar manner and to advocate the view that it is not a dibasic acid in the proper sense of the term but more nearly the inorganic equivalent of lactic acid—a view which is applicable probably not only to all "polybasic" inorganic acids and to carbonic acid but also to "hydrated" basic oxides, moreover the argument we shall advance is one which raises wide issues as to the properties and structure of "salts" generally

Sulphuric acid has been constantly under consideration by one of us since 1870; indeed, the present memoir may be regarded as Part II of a communication made to this Society, in that year (the subject of his thesis for the Ph.D. degree in Leipzig), entitled "Contributions to the History of the Acids of the Sulphur Series."[*] It may be added that a communication which he made to the Chemical Society in the following year[†]—"On the Formation of Sulpho-acids"—actually opens with the statement "Occupied

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[*] 'Roy Soc. Proc.,' vol. 18, p. 502 (1870).

[†] 'Chem. Soc. Journ.,' 1871, p. 172, 'B.A. Report,' 1865, p. 961.

with an investigation into the constitution of sulphuric acid, the views on which are, as is well known, extremely conflicting, etc" Throughout the interval, he has never ceased to pay attention to the acids of the sulphur series Of late years, however, the subject appears to have lost interest, on the theoretical side, in the minds of most chemists, as the habit of writing formulæ in accordance with the fashion which set in at about the time referred to has exercised so great an influence that it has been generally assumed that the problem was solved in favour of the symmetrical formula $SO_2(OH)_2$, which has long been used, without question, as representative of sulphuric acid

In point of fact, the problem was scarcely ripe for solution · considerations such as can now be advanced were not then available , indeed the conception of " an acid " was still a vague one—and it is far from definite yet, notwithstanding the fundamental importance of acids

It must not be forgotten that hitherto we have had no decisive methods of deciphering constitution in the case of the simpler compounds, especially those of elements other than carbon. In the case of carbon, the number of compounds is so immense that it has been possible to put our chemical hypotheses to the test of practice over and over again and the odds are so enormously in favour of our fundamental postulates that we may claim to have devised a symbolic system which is self-contained and a practically complete expression of the facts · whatever change may take place in our views of structure, whatever the extent to which they are modified in course of time, our present symbolic language is so complete that it will only be necessary, probably, to translate its terms into those of the new tongue. But in the case of elements other than carbon, it has not been possible to ring the changes in such a way as to favour one particular view to a preponderating extent · fortunately, new methods are now being developed and, it may be hoped—in view of the remarkable results arrived at by Barlow and Pope, by Laue and by the Braggs, correlating crystalline form with internal structure—that ere long we shall be able to deal even with " simple " substances.

In discussing the nature of acids and the manner in which they act, it is all important to remember the conception embodied in the word oxygen and why it is that one of the gases in air was so named originally · the argument is best stated in Lavoisier's own words ·—[*]

"*Nous avons donné à la base de la portion respirable de l'air le nom d'oxygène, en le dérivant de deux mots grecs, ὀξύς, acide, γείνομαι, j'engendre, parce qu'en effet une des*

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[*] 'Traité élémentaire de Chimie.' See 'Œuvres de Lavoisier,' Tome I, Paris, 1864.

propriétés les plus générales de cette base est de former des acides en se combinant avec la plupart des substances. Nous appellerons donc gaz oxygène la réunion de cette base avec le calorique "

The highest oxides of phosphorus, sulphur and carbon were named by Lavoisier phosphoric, sulphuric and carbonic acid respectively.

His prescience was remarkable. No more significant term has ever been devised, as it is undeniable that oxygen *is* the acidifying principle, *par excellence*, whether or no all acids contain oxygen though many oxides are basic substances, the metals in them being sufficiently positive to overmaster the negative properties of the oxygen, it is true generally that the more highly oxygenated they are, the less they are basic and that, in not a few cases, the addition of oxygen to basic oxides involves ultimately their conversion into acidic oxides

The distinction between acid, base and salt was made very clearly by Lavoisier in the following passage :—

" Les substances acidifiables, en se combinant avec l'oxygène et en se convertissant en acides, acquièrent une grande tendance à la combinaison , elles deviennent susceptibles de s'unir avec des substances terreuses et métalliques et c'est de cette réunion que résultent les sels neutres. Les acides peuvent donc être regardés comme de véritables principes salifiants et les substances auxquelles ils s'unissent pour former des sels neutres comme des bases salifiables."

That the bases were less well understood in his day than the acids is obvious :—

"On ne connaît pas mieux, jusqu'ici, les principes constituants de la soude que ceux de la potasse et on n'est pas même certain si cette substance est toute formée dans les végétaux antérieurement à la combustion L'analogie pourrait porter à croire que l'azote est un des principes constituants des alcalis en général et on en a la preuve à l'égard de l'ammoniaque, comme je vais l'exposer , mais on n'a, relativement à la potasse et à la soude, que de légères présomptions qu'aucune expérience décisive n'a encore confirmées."

But none the less Lavoisier had very clear perceptions of the nature of the process by which salts are formed even from metals—

" Mais il faut observer que les alcalis et les terres entrent purement et simplement dans la composition des sels neutres sans aucun intermède qui serve à les unir , tandis qu'au contraire les métaux ne peuvent se combiner avec les acides qu'autant qu'ils ont été préalablement plus ou moins oxygénés On peut donc rigoureusement dire que les métaux ne sont point dissolubles dans les acides mais seulement les oxydes métalliques Ainsi, lorsqu'on met une substance métallique dans une acide, la première condition pour qu'elle puisse s'y dissoudre est qu'elle puisse s'y oxyder et elle ne le peut qu'en enlevant de l'oxygène ou à l'acide ou à l'eau dont cet acide est étendu c'est-à-dire, en d'autres termes, qu'une substance métallique ne peut se dissoudre dans une acide qu'autant que l'oxygène qui entre, soit dans la composition de l'eau, soit dans celle de l'acide, a plus d'affinité avec le métal qu'il n'en a avec l'hydrogène ou la base acidifiable ou, ce qui revient encore au même, qu'il n'y a de dissolution métallique qu'autant qu'il y a décomposition de l'eau ou de l'acide."

And Lavoisier also had a shrewd suspicion of the nature of bases such as lime, magnesia, baryta and alumina, thus :—

"L'oxygène est donc le moyen d'union entre les métaux et les acides . et cette circonstance, qui a lieu pour tous les métaux comme pour tous les acides, pourrait porter à croire que toutes les substances qui ont une grande affinité avec les acides contiennent de l'oxygène   Il est donc assez probable que les quatres terres salifiables que nous avons désignées ci dessus contiennent de l'oxygène et que c'est par ce *latus* qu'elles s'unissent aux acides   Cette considération semblerait appuyer ce que j'ai précédemment avancé à l'article des terres, que ces substances pourrait bien n'être autre chose que des métaux oxydés, avec lesquels l'oxygène a plus d'affinité qu'il n'en a avec le charbon et qui, par cette circonstance, sont irréductibles   Au reste ce n'est ici qu'une conjecture que des expériences ultérieures pourront seules ou confirmer ou détruire."

The accuracy of this last deduction, it is well known, was established by Humphry Davy in his communications to this Society in 1807–1809

After the introduction of the atomic theory, salts were always formulated as binary compounds formed by the union of two oxides—the acid and the base.   The celebrated dualistic hypothesis advocated by Berzelius merely involved the additional assumption that the acid and the base were held together in virtue of their opposite electrical charges—a conception which was developed later on by Faraday and finally by Helmholtz into the hypothesis of charged atoms and ions, the root-conception of the electrolytic dissociation hypothesis introduced by Clausius and afterwards extended by Arrhenius.

The modern conception of an acid was of slow growth   The view advanced by Lavoisier, that oxygen was the acidifying principle, suffered eclipse when Davy published his celebrated proof that "spirit of salt" was not an oxygen compound but simply a compound of hydrogen with the element chlorine

On this account and because of the "acidic" properties of sulphuretted hydrogen and of hydrogen cyanide, it became customary to recognise two classes of acids—*hydracids* (such as hydrogen chloride) and *oxyacids*   Davy even went so far, in 1815, as to suggest that hydrogen was the characteristic constituent of all acids.   Later on, the acids were classed as hydrogen salts, mainly in consequence of Graham's investigation of the phosphates communicated to this Society in 1833.   Graham, it is well known, came to the conclusion that phosphoric *acid*, P_2O_5, combined with the *base* water in three different proportions to form three different *phosphates of water*   in like manner, he applied the term *sulphate of water* to the compound $H_2SO_4 = SO_3.OH_2$

But the oxides SO_3 and P_2O_5 were long spoken of as acids and the compound SO_4H_2 was commonly termed the monohydrate of sulphuric acid, briefly *monohydrate*, by makers and users of the acid   Gradually, however, the term acidic oxide or anhydride was substituted for that of acid in the

case of such oxides, but even at the present day carbonic acid remains the popular name of carbon dioxide, so that we still have one link with the past.

The issue has been further complicated by the introduction of the ionic dissociation hypothesis According to this, substances such as those represented by the formulæ HCl, HNO₃ and H₂SO₄ undergo "dissociation" when dissolved in water and the constituent common to and characteristic of all acid solutions is the free hydrogen ion · the strength of an acid, it is assumed, depends on the extent to which it thus undergoes dissociation, so that the effective acidity of weak solutions of an acid is commonly spoken of in terms of the concentration of the hydrogen ions. It is not legitimate, therefore, to speak of compounds such as those referred to as acids nevertheless this is still done In 1885, prior to the popularisation of the Arrhenius hypothesis, one of us insisted that hydrogen chloride was not an acid substance in itself and that it acted as an acid only when in conjunction with water * the proposition was then made and has since been often repeated that the term acid should be confined to the solution the term *chlorhydric acid* was advocated as a suitable name for the complex conceived to be present in the solution. The meaning Lavoisier attached to the term acid would be restored if this view were adopted and applied generally all acids would contain oxygen (or an equivalent element in the periodic series) and the acid function would be one conditioned by the presence of oxygen—though not of oxygen alone but of oxygen in association with hydrogen, "acidification" being the consequence of the addition of hydrone.

Having thus directed attention to one of the main issues we desire to raise, we now pass to the consideration of the properties of sulphuric acid

The Properties of Sulphuric Acid

These are peculiar in many ways The anhydride exists in two forms: one of these apparently has twice the molecular weight of the other in this connexion, it is noteworthy that the complex acid chloride $S_2O_5Cl_2$ derived from two molecules of the anhydride, not the simple chloride SO_2Cl_2 derived from a single molecule, is formed by the direct interaction of sulphuric anhydride and carbon tetrachloride as well as in several other similar interactions.

Sulphuric anhydride combines readily not only with hydrogen chloride but also with methylic and ethylic chlorides.

When sulphuric acid is subjected to the action of phosphorus pentachloride, the compound produced, SO_2HCl, is identical with that formed by associating the anhydride with hydrogen chloride: on further treatment with tho

* 'Brit. Assoc. Report,' Aberdeen, 1885, p. 960.

pentachloride, however, the compound which is formed is the complex chloride $S_2O_5Cl_2$, not the simple chloride SO_2Cl_2.

This latter compound is obtained by combining sulphur dioxide directly with chlorine   It is a remarkable fact that both the anhydro-chlorides, SO_2Cl_2 and $S_2O_5Cl_2$, are powerful *chlorinating* agents.

On the other hand, the anhydride and both the compounds SO_3HCl and $S_2O_5Cl_2$ are powerful *sulphonating* agents

Sulphuric acid is commonly regarded as *dibasic*, because it forms both acid and normal sulphates such as are represented by the formulæ $NaHSO_4$ and $Na_2SO_4 \cdot$ but no valid proof of the molecular weight of these salts has been given, hence it is open to us to regard the acid salts as formed either by the displacement of half the hydrogen in a " molecule " of the acid or by the association of a " molecule " of the acid with a " molecule " of the normal or neutral salt.

It is remarkable, that although sulphuric acid is the strongest of acids, the " strength " of the acid, deduced from the molecular electrical conductivity of moderately dilute solutions, is less than 20 per cent. greater than that of chlorhydric and nitric acids: *at high dilutions*, however, the value rises to about double that of the strong monobasic acids.

The molecular hydrolytic activity of sulphuric acid is also greater, though only to the extent of nearly 20 per cent, than that of chlorhydric and nitric acids   But the acid ethereal salts of sulphuric acid and the sulphonic acids are strong monobasic acids only very slightly inferior in strength to chlorhydric and nitric.   This perhaps is the most striking fact to be taken into account in considering the structure of the acid.

It appeared to us that a further study of the sulphonic acids as hydrolytic agents was desirable, in view of the small amount of information extant, especially as they have not been studied hitherto at comparative concentrations nor more than superficially and no attention has been paid to the polysulphonic compounds

It is well known that the properties of benzene itself are greatly modified by the introduction of what may be termed neutral radicles.   The homologous hydrocarbons formed by methylating benzene are all more " active " substances than the parent hydrocarbon   but when halogens or negative compound-radicles such as NO_2 are introduced into benzene its " activity " is reduced. The benzene system, therefore, appears to be a plastic system capable of responding to each and every change that is made in its composition.

When either of the radicles OH and NH_2 is introduced into benzene, the activity rises ; but by introducing hydrocarbon or acid radicles in place of the hydrogen into either of the groups, the influence these radicles exercise

on benzene is altogether modified and reduced · and not only is this the case but there is reason to believe that the oxygen and nitrogen atoms themselves are also modified by such treatment and rendered less receptive. In other words, there is evidence that both the benzene complex and compound radicles such as OH and NH_2 are "plastic" systems and that they are reciprocally affected, when in association, by changes made in either system.

The benzene system is also modified by sulphonation: little is known, however, as to the way in which the sulphonic radicle, SO_3H, is affected by association with a hydrocarbon radicle or by changes made in the hydrocarbon radicle to which it is attached whereas, in the case of carboxylic acids, the strength of the acid is increased by the introduction of negative elements into the radicle with which it is combined, the few cases studied hitherto appear to show that the strength of the sulphonic acids is lowered. Experiments carried out by one of us have shown, however, that modifications so "distant" as those affected by altering the OH group in phenol-parasulphonic acid, $HO\,C_6H_4.SO_3H$, by introducing methyl in place of the hydrogen atom in the hydroxyl group, may modify the properties of the SO_3H radicle—consequently, it would seem that even when three compound systems are associated in a single molecule all are reciprocally affected by a change made in any one of the three.

The Hydrolytic Activity of Sulphonic Acids

The following acids have been used by us ·—

  I Benzenesulphonic acid, $C_6H_5.SO_3H$. tolueneparasulphonic acid, $CH_3.C_6H_4\,SO_3H$ · mesitylenesulphonic acid, $1\cdot3\!:\!5(CH_3)_3\,C_6H_2.SO_3H$.

  II. Parachloro-, parabromo- and pariodobenzenesulphonic acid

  III Paradichloro-, paradibromo- and paradiiodobenzenesulphonic acid

  IV. α-Bromocamphor-β-sulphonic acid

  V. Benzeneortho-, para- and metadisulphonic acid.

  VI. Benzene-1 3.5-trisulphonic acid : toluene-1·3 5 trisulphonic acid

The experiments were all carried out at 25° C.$\pm$0·01° with the apparatus described in parts XII and XXII of this series.* The acid was weighed out in one of the flasks of the mixing apparatus and the sugar and the remainder of the water required to give the desired dilution in the other · before adding the one to the other, each solution was brought to the experimental temperature : the two liquids were then rapidly mixed and the mixture at once transferred to the polarimeter tube, which was already in position and at

* XII, 'Chem Soc. Trans,' 1911, p. 349 ; XXII, 'Roy. Soc. Proc.,' A, vol. 87, p. 539 (1912).

25° C. The amount of sugar used was always small, usually in the proportion of one-quarter of a molecular proportion to one of acid and 50 to 200 of the fundamental molecules of water   in the case of more concentrated solutions one-eighth was frequently used either instead of or as a check on the experiments with one-quarter of a molecular proportion.   As in the previous inquiry, the source of light was the "mercury green" light ($\lambda = 5461$) given by a silica mercury lamp

The final results of all the experiments made are given in Table I. Tables II to VI and VIII contain the full data of the experiments in certain representative cases· as the course of change in other cases was precisely similar and always regular, it is unnecessary to give the details of the experiments, nearly 80 in all.

The velocity coefficient K′ is 10^5 K log e in the equation of mass action $dx/dt = \mathrm{K}(a-x)$ and is deduced by means of the equation (see these Studies, No XII)

$$\mathrm{K}' = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2} \times 10^5,$$

a being the initial concentration of the cane sugar and x_1, x_2 the amount hydrolysed at times t_1, t_2, etc   The differences between the rotations R_1, R_2 at times t_1 and t_2 and the final rotations R_∞ are proportional to the concentrations $(a - x_1)$ and $(a - x_2)$ of the sugar left unhydrolysed at those times.

In the tables, the values of K′, to the nearest whole number usually, are placed opposite the values of the rotations corresponding to the times t_1 · as the interval $t_2 - t_1$ is indicated, it can be seen, therefore, which values of $(a - x)$ were used in the calculation of the constant.   The times of observation were varied according to the conditions of the experiments.   In cases in which hydrolysis took place very rapidly, mean readings were recorded at every 5′ interval, each being the mean of 5 readings taken at the given time, at 1′ and 0·5′ before and at 0 5′ and 1′ after   When hydrolysis was effected slowly, several readings were taken at intervals close together · another set of readings was taken after a long interval of say 60′ and then another similar series after another long interval   These long intervals are used as the $t_2 - t_1$ intervals.   The different values of K′ recorded are all deduced from different readings and have thus no common error ; they refer also to consecutive portions of the interactions and generally do not overlap

Table I.—Molecular Hydrolytic Activity (K') of Sulphonic Acids at Different Dilutions.

Acid "water" ratio A : OH₂	20	40	60	80	100	150	200	500	1000
Sulphuric acid	1380	967	694	497	355	256	117		
Benzenesulphonic acid	1067	713	525	413	297	220	96·9		
Benzeneorthodisulphonic acid				1157	452	273	195		
Benzeneparadisulphonic acid					522	215·3			
Benzenemetadisulphonic acid			1463	734	533	312	220		
1 3 5 Benzenetrisulphonic acid					862	365·5			
Chlorobenzeneparasulphonic acid					499	216	97·7		
Bromobenzeneparasulphonic acid					481	208	95·2		
Iodobenzeneparasulphonic acid					489	214	97·4		
Paradichlorobenzenesulphonic acid					475	209	96·9		
Paradibromobenzenesulphonic acid			484	389	276	212	97·8		
Paradiiodobenzenesulphonic acid					293	223	101·3		
Tolueneparasulphonic acid	1000	677	507	402	283	217·4	96·7	37	18
1:3 5 Toluenetrisulphonic acid					960	361			
Mesitylenesulphonic acid					480	205	92·7		
a-Bromocamphor-β-sulphonic acid						201·3	94·3		

Table II.—Benzenesulphonic Acid.

$C_6H_5SO_5H$ $100 H_2O : 0.25C_{12}H_{22}O_{11}$			
Times of observation	Observed rotation, R	$R - R_\infty$ $(a-x)$	K' $t_2 - t_1 = 60'$
h m s	°	°	
2 30	11 586	15 740	219
32 30	382	536	219
35	·204	358	220
3 0	9 376	13 530	219
2 30	·204	358	220
5	·032	186	219
3 30	7 476	11 630	220
32 30	320	474	220
35	170	324	221
4 0	5 842	9 996	
2 30	708	862	
5	592	·746	
4 30	4 424	8 578	
32 30	316	470	
35	204	358	
Final rotation R_∞	−4 154		Mean 219 7

Table III —Tolueneparasulphonic Acid

$OH_3C_6H_4SO_3H$ $100H_2O$ $0.25C_{12}H_{22}O_{11}$			
Times of observation	Observed rotation, R	$R - R_\infty$ $(a-x)$	K'
h m s	°	°	
1 10	11 600	15 ·711	218
12 30	398	509	217
15	202	313	217 $t_2 - t_1 = 40'$
17 30	·014	125	217
20	10 826	14 937	217
1 50	8 ·744	12 ·855	217
52 30	584	·695	217
55	428	539	217 $t_2 - t_1 = 70'$
57 30	728	389	218
2 0	·116	227	217
3 0	4 ·956	9 ·067	
2 30	836	8 947	
5	·722	·833	
7 30	·612	·723	
10	500	611	
Final rotation R_∞	−4 ·111		Mean 217 4

Table IV —Mesitylenesulphonic Acid.

(CH₃)₃C₆H₂SO₃H : 100H₂O 0·25C₁₂H₂₂O₁₁			(CH₃)₃C₆H₂SO₃H 200H₂O : 0·50C₁₂H₂₂O₁₁		
Times of observation	Observed rotation, R	K'	Times of observation	Observed rotation, R	K' $t_2-t_1=240$
h m s	°		h m s	°	
3 45	11 790	202	1 0	12 ·620	
47 30	606	202	2 30	530	
50	432	201 t_2-t_1	5	442	
52 30	252	200 $=75'$	7 30	348	
55	068	202	10	252	93 1
			12 30	·166	93 1
4 0	7 118	204	15	·076	92 8
2 30	6 ·996	204			92 6
5	886	204 t_2-t_1	5 0	5 878	92 5
7 30	·736	203 $=120'$	2 30	822	92 5
10	606	202	5	784	92 4
			7 30	738	
6 0	2 296		10	690	
2 30	234		12 30	636	
5	160		15	·588	
7 30	100				
10	034				
Final R∞	−4 ·075	Mean 202 5	R∞	−4 150	Mean 92 7

Table V —1 3 5 Benzenetrisulphonic Acid

C₆H₂(SO₃H)₃ 100H₂O 0 25C₁₂H₂₂O₁₁		
Times of observation	Observed rotation, R	K' $t_2-t_1=30'$
h m	°	
5 0	9 434	979
5	7 ·978	981
10	6 670	983
15	5 502	984
20	4 456	977
25	3 520	983
30	2 684	984
35	1 ·932	
40	1 ·260	
45	0 ·666	
50	0 146	
55	−0 386	
6 0	−0 ·764	
Final R∞	−4 304	Mean 982

Table VI —$C_6H_4(SO_3H)_2$ 100 OH_2 0·25 $C_{12}H_{22}O_{11}$

Benzenemetadisulphonic Acid

Times of observation	Observed rotation, B	K'
h m	°	
3 25	7·664	539
30	·012	538
35	6·356	535
40	5·728	534
8 5	3·240	533
10	2·816	535
15	·404	534
20	·024	533
4 5	−0·424	533
10	·644	
15	·332	
20	−1·008	
5 10	−2·288	
Final B∞	−8·800	Mean 533

$t_2-t_1=40'$ (first group); $t_2-t_1=60'$ (second group); $t_2-t_1=60'$ (533)

Benzeneparadisulphonic Acid

Times of observation	Observed rotation, B	K
h m	°	
12 15	8·478	522
20	7·764	521
25	·102	525
30	6·486	522
12 55	3·794	517
1 0	·960	524
5	2·928	522
10	·530	524
1 55	−0·078	
2 0	·322	
5	·522	
10	·726	
Final B∞	−3·780	Mean 522

$t_2-t_1=40'$; $t_2-t_1=60'$

Benzeneorthodisulphonic Acid.

Times of observation	Observed rotation, B	K'
h m	°	
2 45	10·030	449
50	9·304	453
55	8·818	452
8 0	7·964	452
3 25	5·196	453
30	4·692	452
35	·248	452
40	3·818	453
4 25	0·818	
30	·558	
35	·316	
40	·066	
Final B∞	−4·210	Mean 452

$t_2-t_1=40'$; $t_2-t_1=60'$

Discussion of the Results.

Order of the Interaction —A point of interest, to which attention may be directed in the first place, is the fact that the rate at which the action proceeds in all cases is strictly that of a so-called unimolecular change, not only in the case of the monosulphonic acid but also in the case of each of the di- and of each of the tri-sulphonic acids.

Whatever the explanation may be of the changes involved in the phenomena of hydrolysis, it is to be supposed that the rate at which the interactions proceed under the influence of a polysulphonic acid will be that at which " unimolecular " changes are effected so long as each effective acidic centre acts independently ; the results we have obtained are, therefore, proof that although the interaction involves one molecule of acid and either two or three of sugar, as the case may be, the sugar molecules are attacked separately, so that the " basicity " of the acid is in no way disclosed (*cp* XXII, p 570)

The molecule of a polysulphonic acid is to be pictured, in fact, as capable of acting simultaneously on as many separate, independent molecules of sugar as it contains sulphonic radicles, so that the activity of the disulphonic acid is to be thought of as exercised from a single centre equally in two directions and that of the trisulphonic acid as exercised equally in three directions

Strength of the Acids —The benzenepolysulphonic acids are all of extraordinary strength, the metadisulphonic acid being molecularly more than twice and the trisulphonic acid more than thrice as strong as the monosulphonic acid and all but four times as strong as sulphuric acid at the concentration A $100H_2O$ *

If, however, the concentration of benzenemetadisulphonic acid and of benzenemetatrisulphonic acid be expressed in terms of equivalents instead of in molecular proportions, the activities of the mono-, di- and tri-sulphonic acids are the same at *equivalent* strengths. On reference to Diagram A, it will be seen that the values of the three acids all fall on one curve (that of benzenesulphonic acid) In other words, the sulphonic unit (SO_3H) has the same value in each of the three acids when the amount of water used in proportion to each unit is the same

The explanation of the fact that the molecular activity of the disulphonic is more than twice, that of the trisulphonic acid so much more than thrice, that of the monosulphonic acid at corresponding concentrations is that each SO_3H group has a large concentrating or—to use the term adopted by recent

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* In view of this result, it is conceivable that the extreme activity of some enzymes, invertase, for example, is in part due to the existence of several active centres at the surface of the colloid complex, not merely to the weakness of the specific hydrolyte with which alone it is compatible

workers—salt effect the amount of "free" water present in the case of the di-
and trisulphonic acids is, therefore, very much less than in the case of the

Dia. A.
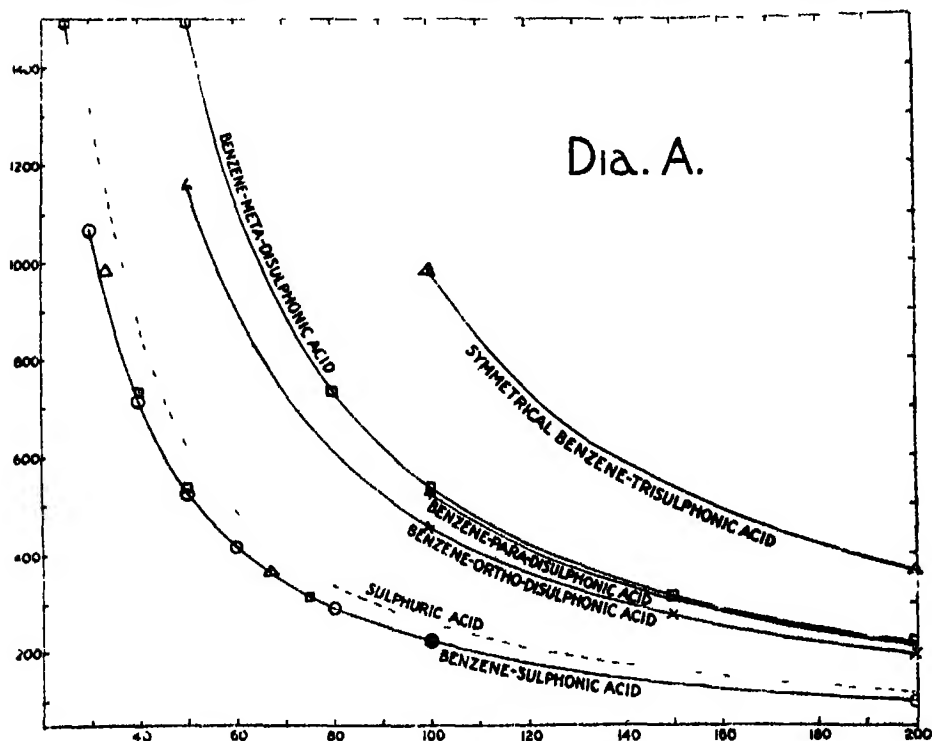
monosulphonic acid when the same amount is used per molecule in dissolving
the acid

If the concentrating or "salt" effect of the acid be expressed as the
"apparent hydration value," in the manner adopted in previous communi-
cations of this series, the values obtained in the case of benzenemeta-
disulphonic acid are much greater than those assigned to the monosulphonic
acid and approach to twice their magnitude at the higher dilution (see
Table VII)

Too much importance should not be attached to the actual numbers in this
Table, as a very small error in the velocity coefficients used in deducing the
values makes a large difference in the apparent hydration values , it is clear,
however, that the values are much greater in the case of the disulphonic acid

Influence of Constitution on the Strength of the Acid.—The paradisulphonic
acid is slightly and the orthodisulphonic acid considerably weaker than the
metadisulphonic acid. This result is one of some significance. It has long
been recognised that if two radicles are present in the para-position in benzene

Table VII.

Total H_2O	Apparent hydration values	
	Monosulphonic acid	Metadisulphonic acid
30	9 2	—
40	11 2	—
50	12 8	18 4
60	13 6	21 ·0
70	14 4	23 2
80	15 0	25 3
90	15 5	27 ·0
100	16 0	28 0

they mutually influence each other and that this is still more the case when they are present in the ortho-position, whilst radicles relatively in the meta-position have little or no influence upon one another   Apart from any such mutual influence, the very considerable lowering in activity manifest in the case of the ortho-acid, however, may also be due to the fact that, in the case of this acid, the separate activities of the two sulphonic radicles cannot be so freely exercised as in the case of the other acids because of their proximity and the consequent difficulty the sugar molecules have in " crowding in " upon them.

The influence of halogens appears to be remarkably slight and out of all proportion small in comparison with that which they exercise in the case of carboxylic acids.   Probably this is a result of considerable significance   The order in which the three halogens exercise an influence is not the same, however, in the mono- and di-substituted derivatives; in the case of the former, the activity is very slightly below that of the unsubstituted acid and bromine has the greatest influence in depressing the strength,[*] in the case of the latter, chlorine and bromine both depress the strength whilst iodine raises it slightly.

The influence of methyl, as shown in tolueneparasulphonic acid and still

[*] The experiments at the dilution A 50 H_2O were repeated in the case of the chloro- and bromo-acids but the values of the velocity coefficients obtained were the same as previously, viz. 499 and 481 respectively   A sample of the chloro-acid was then prepared from the sulphochloride and on carrying out an experiment at the dilution A · 100 H_2O the value first obtained was confirmed   No explanation of the irregular order of the activities of the three acids can be given at present : it would appear, however, that the order observed is the correct one, as crystallographic measurements of the sulphochlorides of the three acids, which Mr Mummery has made, show that the a-axis has a lower value in the bromo- than in either the chloro- or the iodosulpho-chloride, which are practically identical in their dimensions.

more in mesitylenesulphonic acid, is depressant [*]   Methyl has a similar influence in the case of the trisulphonic acid   It is a striking fact that bromocamphorsulphonic acid falls very little short of benzenesulphonic acid in strength

Taking the results generally into account, it is clear that the strength of the sulphonic radicle is affected only to a relatively slight extent when alterations are made in the hydrocarbon radicle to which it is attached, but that it is subject to some modification, there can be no doubt, in view not only of the differences in strength that are manifest but also of other differences such as solubility, thus paradibromobenzenesulphonic acid is relatively slightly soluble and crystallises with extreme facility in comparison with the unsubstituted acid

Variation in Strength on Dilution—It will be noticed that as dilution proceeds the acids tend to behave more and more alike, it is therefore probable that the values per unit of SO_3H would not be very different at sufficiently low dilutions   The change is doubtless in part due to the gradual disappearance of the "concentrating or salt effect," already referred to, which the acid exercises in the more concentrated solutions, it may be also in part due to gradual depolymerisation of more complex molecules: such differences, between the various acids, however, could only be the outcome of constitutional peculiarities of the fundamental molecules and may therefore be regarded as an indication that the sulphonic radicle is more or less responsive to variation in the radicle with which it is associated

An experiment was carried out, which is recorded in Table VIII, in which equal molecular proportions of benzenesulphonic acid and of toluenepara-sulphonic acid were used as the hydrolyst, the assumption being made that, in the event of each acid existing in solution as a polymerised molecule, the two acids might mutually interfere and each molecule be to some extent depolymerised   in this case, it was to be expected that the strength of each acid would be more or less raised and the strength of the mixture in excess of the calculated mean

The result shows that the effect produced by the mixture is exactly the mean of the effects produced by the two acids separately

This result, however, cannot be regarded as final proof that the acids are not present in a polymerised state, unless it be assumed that the molecules of the two acids are sufficiently incompatible to be incapable of associating together   As there is reason to suppose that, in some cases at least, the

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[*] We are inclined to regard the value arrived at in the case of mesitylenesulphonic acid at a dilution of 200 as too low

Table VIII —40H$_2$O ($\frac{1}{2}$C$_6$H$_5$.SO$_3$H + $\frac{1}{2}$CH$_3$.C$_6$H$_4$.SO$_3$H) 0·25C$_{12}$H$_{22}$O$_{11}$

Times of observation	Observed rotation, R	K' $t_2 - t_1 = 50'$
h m s	°	
11 40	16 788	695 8
42 30	15 756	696 3
45	14 786	696 1
47 30	13 776	695 ·8
50	12 856	696 4
52 30	11 ·974	697 1
55	11 121	697 8
		Mean 696 5
12 30	2 ·094	
32 30	1 626	C$_6$H$_5$ SO$_3$H 715 6
35	1 170	CH$_3$ C$_6$H$_4$ SO$_3$H 677 2
37 30	0 ·744	
40	0 324	Mean 696 4
42 30	−0 060	
45	−0 470	
Final R$_\infty$	−9 87	

molecules of a benzenesulphonic acid form triplets[*] and that two isomorphous acids might well crystallise together, this assumption cannot at present be made with any degree of certainty   It will be desirable to carry out similar experiments with a mixture of incompatible acids—perhaps one of benzene-sulphonic acid with a camphorsulphonic acid would satisfy this condition

Comparison of Sulphonic with Carboxylic Acids —The similarity in behaviour of the various acids we have examined, the almost constant " strength " of the sulphonic radicle, is in striking contrast with the inconstancy of behaviour which is manifest in the case of carboxylic acids

The difference is well brought out in the following table of velocity coefficients originally given by Ostwald in 1883 as representing the hydrolytic activity of various carboxylic acids in volume normal solutions determined by means of methylic acetate —

Chlorhydric	acid . ..	100 000
Formic	„ . .	1 310
Acetic	„	0 345
Propionic	„ .	0 304
Butyric	„	0 299
Isobutyric	„	0 268
Chloracetic	„	4 300

* *Cf.* E. H. Rodd, "The Crystalline Form of Sulphonates," 'Roy. Soc. Proc.,' A, vol. 89, p. 303 (1913).

Dichloracetic acid .	.	23 040
Trichloracetic	,,	.	68 200
Lactic	,,	..	0 901
Trichlorolactic	,,	.	6 900
Pyruvic	,,		6 700
Oxalic	,,		17 46
Malonic	,,		2 87
Succinic	,,		0 496
Tartaric	,,		2 296
Malic	,,		1 181
Citric	,,		1 035

An explanation of the difference is to be found probably in two directions Whatever tendency there may be in the sulphonic acids to undergo polymerisation, it appears probable from the behaviour of such acids in general that the complex molecule is easily broken down in presence of water and that the acid soon reaches a high degree of activity if not its maximum possible strength

The depolymerisation of carboxylic acids, on the other hand, appears to take place, as a rule, with extreme slowness and to approach completion only at high dilutions—and the structure of the polymerised molecules is such apparently that they have little " strength " as acids

In the second place, the sulphonic radicle appears to have an almost constant acidic value, whatever its associate may be　The carboxylic radicle, however, seems to vary greatly in acidic power and is presumably more " plastic " than the sulphonic radicle　it is difficult to account for the extraordinary difference in behaviour manifest between acetic acid and its chlorinated derivatives, for example, on any other assumption, though the introduction into acetic acid of chlorine in place of hydrogen may well render the molecules less prone to undergo polymerisation in aqueous solution, owing to the increased tendency of the fundamental molecules to combine with water rather than with each other—so that the difference between acetic and trichloracetic acid may be due, in no small measure, to the fact that the former is present mainly in the polymerised inactive form whilst the trichlorinated acid is present in the form of simple molecules

It is difficult to believe that the free carboxylic radicle, COOH, has an activity comparable with that of the SO_3H radicle in the sulphonic acids · the facts generally appear to be more in harmony with the view that it has a fluctuating value and that its intrinsic strength is largely a question of the nature of its associate.

In view of the assumption that is often made that carbonic acid is hydroxyformic acid, it may be pointed out here that its extreme weakness is against this view as it should be stronger than formic acid, if so constituted, especially as there is no reason to believe that it exists in solution in a polymerised form *

The Constitution of Sulphuric Acid

Taking into account the properties generally of the acid—particularly the fact that the "strength" of the acid-ethereal-sulphates and of the sulphonic radicle (SO_3H) in sulphonic acids is so considerable and not far removed from that of sulphuric acid itself—there is little to support the view that sulphuric acid is a dibasic acid in any proper sense of the term, there is much, however, to justify the conclusion that its primary behaviour is monacidic and, in fact, that of a very strong "monobasic" acid Apparently, however, at high dilutions, it is capable of manifesting a second but quite different order of activity

The symmetrical formula commonly attributed to sulphuric acid, $SO_4H_2 = SO_2(OH)_2$, not only does not correspond with the behaviour of the compound even as an acid but it may be asserted that not a single interaction is known which renders the adoption of such a symbolic expression necessary

At the outset, sulphuric acid was formulated by Williamson, on the water type, as derived from two molecules of water—

$$\left.\begin{array}{c}H\\H\end{array}\right\}O \qquad \left.\begin{array}{c}H\\H\end{array}\right\}O \qquad\qquad \left.\begin{array}{c}H\\SO_2\end{array}\right\}O \qquad \left.\begin{array}{c}\\H\end{array}\right\}O$$
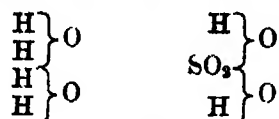
in consequence of its presumed relationship to the two chlorides SO_3HCl and SO_2Cl_2 · when considerably later, mainly through Frankland's influence, resolved structural formulæ came into vogue, this formula became—

$$O\diagdown\!\!\!\diagup OH$$
$$O\diagup S\diagdown OH$$
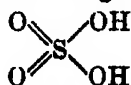
The formation of sulphuric acid from sulphuryl chloride, SO_2Cl_2, is not necessarily a proof, however, that the acid contains two (OH) groups, as it may be equally well supposed either that the chloride is directly convertible into the acid, thus :—

$$SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl,$$

or that it is primarily resolved into sulphurous acid and chlorine, which

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* *Cp.* 'Ber deut Chem. Ges.,' 1914, p. 945

interact, *in statu nascendi*, giving rise to sulphuric acid and hydrogen chloride :—

$$SO_2Cl_2 + OH_2 = SO_3H_2 + Cl_2,$$
$$SO_3H_2 + OH_2 + Cl_2 = SO_4H_2 + 2HCl$$
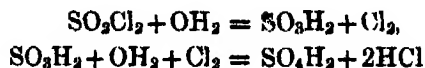
In like manner, the formation of the chloride SO_3HCl is not necessarily a proof of the presence of an OH group in the acid, as the primary action of phosphorus pentachloride may be merely to " dehydrate " the acid —

$$SO_4H_2 + PCl_5 = SO_3 + POCl_3 + 2HCl$$

Whilst there has been agreement as to the hydroxylic character of the acid, the general structure has been the subject of considerable argument—Kekulé, who consistently maintained the doctrine of constant valency and held that sulphur was a dyad, represented the acid by the formula :—

$$HOOSOOH.$$

It has also been represented by the formula—
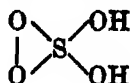
in which sulphur appears as a tetrad element   And that sulphur does sometimes function as a tetrad follows from the proof given by Pope and Peachey[*] that compounds of the type $(R R_1 R_2)S.X$ are optically active, but there is no satisfactory evidence that it ever has a higher valency, though it is often asserted that the hexad character of the element is established by the existence of a hexafluoride, SF_6 The peculiar properties of this compound are better accounted for, however, by the assumption that the fluorine atoms form a closed system   the fluoride cannot well be used, therefore, as a proof of the valency of sulphur

The discussion entered on a new stage when Barlow and Pope advanced the proposition that the " volume sphere of influence " (Valency-volume) of sulphur, like that of oxygen, is never more than about twice that of hydrogen

Having formed the opinion that sulphuric acid is a monacidic compound like the sulphonic acids, we have been led to consider the problem of the structure of the sulphonic acids and of sulphuric acid with reference to the crystalline structure of the sulphonic compounds, from the point of view dealt with in the communication on this subject by Armstrong, Colgate and Rodd (*op* these ' Proceedings,' *seq.* pp 111–173).

We shall base our arguments on the assumption that sulphur, like oxygen, whilst potentially a tetrad, usually functions as a dyad.

[*] ' Trans. Chem. Soc.,' vol 77, p. 1072 (1900).

In the model of benzenesulphochloride shown in fig 1, the sulphur atom is represented as connected with a (masked) carbon atom in the lower tier of atoms comprising the benzene unit and also as separately combined with two oxygen atoms which are not in direct connexion · the chlorine atom lies between these two oxygen atoms and presumably serves to connect them ·
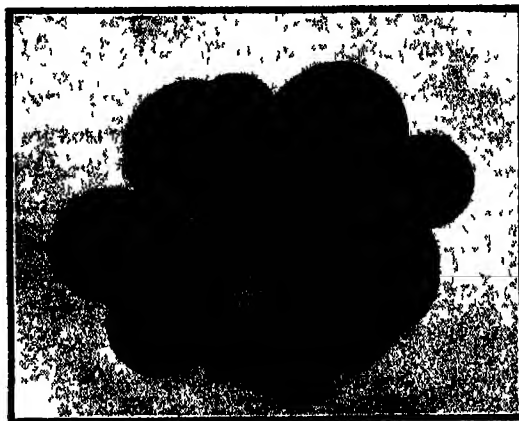
Fig 1 —Model of Benzenesulphochloride

but—assuming that the four affinities in oxygen and sulphur are directed tetrahedrally—there is no spare affinity of the sulphur atom in the direction of the chlorine atom . this, however, as well as the sulphur atom, has an affinity unsatisfied   In the solid compound, these spare affinities may operate in promoting the combination of the units in the crystalline substance , in solutions they may be in association with units of the solvent.

The unit of the sulphonic acid is obtained from that of the chloride by substituting the " triad " compound radicle OH for the triad simple radicle Cl

The method of constructing an assemblage representing the crystalline structure of a compound substance introduced by Barlow and Pope consists in causing two or more units, each representing in composition and configuration one component of the compound, to interlock, the several component assemblages being intercalated homogeneously in such manner that the cavities formed in the one are occupied by the groups present in the others.

Conversely the structural units representing the several components of a compound molecule can be traced in and dissected out from the assemblage representing the crystalline structure of the substance.   The important result to which we are permitted to call attention is that on applying their method to the sulphates, Messrs. Barlow and Pope have been led to formulate these salts crystallographically as compounds of the type $SO_3 OR_2$, not as

compounds of the hydroxylic type, $SO_2(OH)_2$· a return is thus suggested to the view originally introduced by Lavoisier and consistently advocated by Berzelius   Apart from the crystallographic evidence favouring this mode of treatment, the correctness of the view is also indicated by the existence of the well-defined hydrates $2SO_3 OH_2$, $SO_3 OH_2$, $SO_3.2OH_2$ and of stable salts such as $Na_2S_2O_7$, Pb_2SO_5 and Hg_3SO_6, corresponding to them, as well as by the fact that the ordinary salts of telluric acid are derived from the hydrate $TeO_3 3H_2O$ *

The model shown in fig 2 and in projection in fig. 3a embodies the conception referred to and appears to us to be a satisfactory expression of the chemical behaviour of the acid.
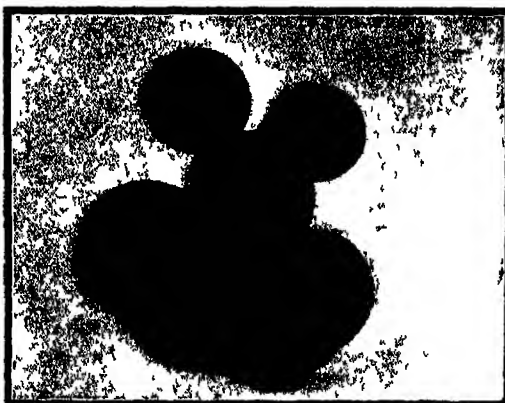
Fig 2 —Model of Dihydrogen Sulphate (Sulphuric Acid), $SO_2 OH_2$

· In the model, the sulphur atom exercises the function of a dyad   it may be supposed either that two affinities of the atom are latent or—as there is reason to believe that the acid is an "associated" substance—that they serve to maintain the connexion between two or more units such as that shown

Two only of the oxygen atoms are in direct connection with the sulphur atom but a third atom serves to unite them, so that the complex SO_3 forms a closed system   In the "acid," the two oxygen atoms adjoining the sulphur atom are further united by the radicle OH_2, leaving each with an affinity "free" but in the plane below that in which the OH_2 group is situated.

The attachment of a second OH_2 to the same two oxygen atoms in this lower plane may be supposed to give rise to the monohydrate of sulphuric

* The crystalline hydrate $SO_4H_2.4H_2O$ is perhaps formed by the union of $3H_2O$ *en bloc* with the monohydrate $SO_4H_2.OH_2$ in fact, the possibility that the complex hydrates are formed by the inclusion of one or other of the polyhydrones (these Studies, No. VI) in the crystalline structure is obviously one that must be taken into consideration in future discussions of the constitution of hydrates.

"acid ". or this second hydrate might be formed by the attachment of OH₂ to what may be termed the median oxygen atom of the SO₂ unit It is equally conceivable that the first and second hydrates may be formed in the reverse order

It is noteworthy that while the " fixation " of the first molecular proportion of hydrone by sulphuric anhydride involves the evolution of 21,320 units of heat, that of the second affords 6379 and that of the third only 3039 units the additional amount of heat given out on continuing the dilution is eventually about equal to that evolved on first mixing the acid with two molecular proportions of water and the whole amount evolved on dissolving the " acid " (H_2SO_4) in water is less than that evolved on converting the anhydride into the acid.

A distinction of consequence is to be drawn between the manner in which the OH₂ radicles become attached to the anhydride the first may be regarded as directly associated without alteration, the second—that which unites with the median oxygen atom—may be supposed to be " distributed " as it enters into combination, so that this oxygen atom is " hydrolated," to use the term introduced by one of us in No VI of these Studies * The median oxygen atom, therefore, has specific properties and we are inclined to regard this as the " centre of activity " in the molecule of the acid hence also perhaps the behaviour of the acid—*its essentially monacid character* The properties of oil of vitriol are such as to favour the view that the compound H_2SO_4 is polymerised readily and that dilution is a process of depolymerisation It is probable, in fact, that the gradual increase in the activity of the acid, as shown by the rise in molecular conductivity as dilution proceeds, is a consequence of the gradual " unmasking " of the sulphur atom and due to its more or less complete " hydrolation "

The active units in a solution of the acid are presumably either of the type shown in fig. 3*b* or the correlate of this compound which is formed by the distribution of the acid molecule against the hydrone molecule or it may be that in concentrated solutions two such units act together and that when the solution is diluted the complex is gradually resolved into " hydrolates " of the form shown in fig. 3*c*

On such an assumption it is possible to understand the considerable increase in molecular electrical conductivity which attends the dilution of sulphuric acid, on account of which it is apparently to be ranked as a dibasic acid.†

* 'Roy. Soc. Proc.,' A, vol. 81, p. 80 (1908).

† If it be supposed that sulphuric acid is diacidic even in concentrated solutions, the equivalent strength of the acid will be but little more than half that of either nitric or

Two conclusions that are necessary if our view of the constitution of sulphuric acid be correct should be mentioned here   One is that the formation of anhydrous sulphates of the metals is to be regarded as an indirect process . not as the outcome of the direct displacement of one or both

Fig 3
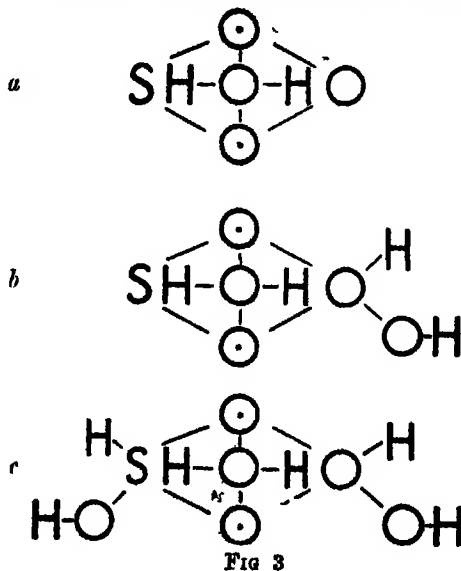
hydrogen atoms but as a process of isomeric change in which the metal passes into a final position of rest from the position it assumes in the hydrolated molecule at entry, the other is that the sulphonic acids are not directly derived from sulphuric acid but are compounds of a distinct type—a conclusion of some interest and importance in connexion with the superior strength of sulphuric acid in comparison with the monosulphonic acids.

In the formula we have suggested, the active " centre" in sulphuric acid is the third atom of oxygen by the addition of which the weakly acidic sulphur dioxide is converted into the intensely acidic sulphur trioxide, the cause of the great difference in behaviour of sulphuric in comparison with sulphurous acid is therefore brought to expression in the formula.

The views here put forward may be applied to other " acids," especially to carbonic, silicic, phosphoric and arsenic acids.   These probably are all to be regarded as compounds of the anhydrides with hydrone rather than as hydroxylic derivatives   though *polybasic*, they are all essentially *monacidic*, like sulphuric acid.

chlorhydric acid.   Such a conclusion is altogether improbable in view of the properties of the compound , moreover, it must then be supposed that it is potentially tetracidic in weak solutions, to account for the increase in its molecular electrical conductivity on dilution.

The Nature of Acidity.

If the term acid is to be attached to the chemically active substance in an acid solution, it is not logical to speak either of the halhydrides or of compounds such as are represented by the formulæ NO_3H and SO_4H_2 as acids—the acid being the product formed in solution by the interaction of solvent and solute

It is therefore of primary importance that we should seek an agreement as to the nature of the processes of dissolution and of "acidification" The conception that the dissolved substance is directly dissociated into electrically charged ions, introduced by Clausius, which Arrhenius has done so much service by carrying to a logical issue, cannot be accepted in its original form, as it is impossible to admit that the solvent acts merely as a screen and that the separate ions are present and move about freely in the solution, being kept apart by the mere interposition of the neutral molecules of the solvent

Moreover, it cannot well be supposed that the ions are torn asunder owing to the attractions exerted by the molecules of the solvent and that they move about separately in the liquid in a hydrated condition ; such an assumption involves the conclusion that the influence of the charges by which, *ex hypothesi,* the ions are held together is overcome by superior force and this could only happen if the ions gave up their charges in combining with the solvent molecules, by so doing, however, they would necessarily lose the magic attribute which gives them the special properties they possess in the eyes of the dissociationist.

It is impossible, in fact, to grant more than potential freedom—superior attractive power—to the ions , this is secured by the hypothesis advocated by one of us from 1885 onwards and ultimately developed in 1908 (No XI) into the view that the molecules of solvent and of solute are equally concerned and that the active "substance" is compounded of the two agents

Every chemist is both taught and prepared to believe that ammonia and hydrogen chloride give rise to ammonium chloride $\left(H_3N < {H \atop Cl}\right)$ and that ammonia and hydrone give rise to ammonium hydroxide $\left(H_3N < {H \atop OH}\right)$ in other words, that hydrogen chloride and hydroxide both become divided up or dissociated at a nitrogen surface and that their radicles or "ions" combine separately with the nitrogen atom.

It is only necessary to extend the doctrine to the formation of acids, bases and "salts" generally.

To take the case of hydrogen chloride, if it be supposed that it becomes

active *as an acid* when dissolved in water because the reciprocal interactions take place which are pictured in the equations

$$HCl + OH_2 = HCl \substack{H \\ < OH}$$

$$H_2O + HCl = H_2O \substack{H \\ < Cl}$$
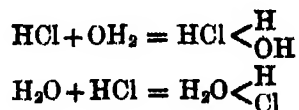
the degree of "activation" will depend on the extent to which such changes are carried In the case of a weak substance, like ammonia or "acetic acid," such changes take place presumably to a minimum extent, in the case of strong agents, such as hydrogen chloride and sulphate, they are at a maximum. The extent to which *relatively* the one or the other of the two reciprocal changes takes place must be supposed to be determined mainly by the relative concentration of the two substances

No distinction can be drawn, from this point of view, between the concentrations of the "ions" of an acid—they are necessarily present in equivalent amounts To speak of the effective acidity of an acid solution in terms of the concentration of the hydrogen ions, is to give an altogether misleading impression , and if, as we believe, acidity be a complex function, it can only be determined by some practical test the result should be reported, therefore, in terms of an accepted practical standard, not in terms of a purely hypothetical interpretation

Enzymes, which simulate acids as hydrolytic agents and surpass them in activity, are beyond all question agents which act selectively in virtue, it must be supposed, of specific qualities, not because they contribute "hydrogen ions" but there is no less reason to believe that acids act in virtue of their specific characters and as wholes than there is to believe that enzymes act specifically The hypothesis that the characteristic activity of acids is due to the hydrogen ion and to this alone and the activity of alkalies, in like manner, to the hydroxyl ion—because the hydrogen and the hydroxyl ion respectively are common, the former to all acids, the latter to all alkalies—is one, in fact, which it is difficult to treat seriously It is as improbable and as much in opposition to our general experience as is the primary hypothesis of the dissociationist school that the ions fall apart immediately a potential electrolyte is dissolved in water. Moreover that the addition of oxygen or the introduction of chlorine in place of hydrogen (in the well known case of trichloracetic acid, for example), should make a compound a stronger acid by rendering it more prone to part with hydrogen is inconceivable.

Unfortunately, qualities are of no account in the eyes of the physical chemist of to-day. Hence it is that it has been customary of late years to regard hydrogen chloride and water as entirely unrelated substances and that

it has been seriously assumed that when the two are mixed together the molecules of the one remain almost all unchanged whilst those of the other are almost all dissociated into their ions. The chemist who takes facts generally into account cannot possibly admit that any such distinction exists

In our opinion, the acidity of an acid is a function of the acid molecule as a whole—of its "ions" collectively and co-operatively—not of one of its parts taken singly or separately and apart from the other, in all cases, moreover, the presence of water (or rather of its fundamental molecule, hydrone) is essential to the formation of the acid proper.

The hypothesis we advocate is in accord with all the ordinary canons of the chemist's belief, inasmuch as it involves the assumption that the two necessary constituents of an acid electrolyte interact reciprocally and give rise to two compounds, thus—

$$HX{<}^H_{OH} \quad \text{and} \quad H_2O{<}^H_X$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
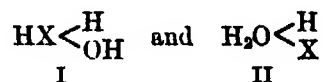
so that both are "ionized," not one of them only.

The proportions in which the two "reciprocals" are present will depend upon the concentration and, assuming that both play their part, the manner in which change takes place under their influence will depend both on the relative and on the absolute proportions in which they are present If it be assumed that the oxonium compound (II) is present in major proportion in concentrated solutions of hydrogen chloride, for example, it follows that this is at least the more active agent in promoting hydrolytic change On the other hand, the assumption that the chloride is "hydrolated" to the maximum extent in dilute solutions would serve to explain the fact that the molecular conductivity of the hydrogen chloride rises to a maximum as the solution is diluted

From such a point of view, it is possible perhaps to explain the lack of agreement in the results given by the hydrolytic and electrolytic methods of contrasting acids In the case of acids of the same degree of basicity, all have very nearly the same activity in sufficiently dilute solutions, judging from their molecular electrical conductivities · but they are found to differ very greatly in strength when their behaviour as hydrolytic agents is determined. If it be assumed that conductivity depends merely on the extent to which the molecules are brought into action owing to their arrangements in chains, without reference to the stability of or to the attractions existent within the chains that are formed, it is not difficult to understand that the behaviour of acids should be more nearly alike the more completely the molecules are brought into line and arranged in

conducting chains   but strength (in an acid) may be supposed to depend merely on the degree of affinity—the attractive power—which the acid radicle has for the hydrolyte   it may well be therefore that of the reciprocal forms present in the electrolyte that of the oxonium type is the essential agent in cases of hydrolytic change and that the compounds of this type formed from different acids differ more or less in strength   Conductivity, in other words, is less a measure of strength than of continuity of action—as in the case of a series of individuals passing buckets of water to put out a fire everything depends on the formation of the "chain"   the individual units may be either weak or strong , provided they act together in unison and continue to pass the buckets along, they are effective agents, though the rate at which and the extent to which they are effective is necessarily limited by the degree of activity exercised by the weakest member of the series

In an alkaline solution, there will be two positive ions present, hydrogen and the metal, in numbers equal in sum to the number of hydroxyl ions   in an acid solution, two negative ions, in numbers equal in sum to the hydrogen ions

According to our view, both constituents of a solution play an active part to the present day, the advocates of ionic dissociation think only of the solute as active.   Consequently, by paying attention only to two ions—hydrogen and the one negative acid radicle, in the case of an acid—they have arrived at the illogical conclusion that the positive and negative ions convey the current in different proportions · had they taken into account the part played by both negative radicles (or in the case of alkalies, that played by the two positive radicles concerned), it would have been realised that no such difference exists and that a factor of extreme importance has been overlooked

Studies of the Processes Operative in Solutions. XXXII —The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids a Contribution to the Discussion on the Influence of Neutral Salts.

By Henry E. Armstrong (F R S) and F P Worley (D Sc)

The manner in which the hydrolytic activity of an acid is affected by the presence of a neutral salt of the acid has been under consideration thoughout this series of Studies In most of the experiments, to limit the number of factors as far as possible and in order that the results might be directly comparable, the salt has been made the only variable The salts used have been either halides or nitrates

The sulphonates are specially suited for such an inquiry on account of the strength of the acids from which they are derived and their rigid neutrality moreover, as a rule, they are sufficiently soluble

The present communication has reference to the influence on the activity of tolueneparasulphonic acid of potassium, calcium, strontium, barium, zinc and cadmium tolueneparasulphonate the magnesium salt was not sufficiently soluble to permit of its use at the degree of concentration adopted in the case of other salts. The activity of the acid was determined at $25° \pm 0\ 01$ by means of cane sugar

It is unnecessary to give the results in detail, as they are in every respect similar to those quoted in the previous communications and the course of change was in all cases regular. The final results are given in Tables I–III and in Diagrams B, C, which show (a) the effect produced by the potassium salt when used in different proportions · (b) the effect produced by the potassium salt in presence of different proportions of acid (c) the effects produced by a variety of salts.

On reference to Table I, it will be noticed that the effect produced by the salt is reduced practically to a third by halving the concentration of the solution: at present, we have no explanation to offer of this remarkable result It may be peculiar to the potassium salt or to tolueneparasulphonic acid. From Table II it will be apparent that the salt has the greater influence the smaller the proportion of acid present. Table III shows that the effects produced by equivalent amounts of the various salts examined are not very different: it will be noticed that the volumes of the solutions are also not very different

Table I—Hydrolysis of Cane Sugar by Tolueneparasulphonic Acid in presence of Potassium Tolueneparasulphonate

Acid	Sugar	"Water" OH₂	Salt	K'	Increase per molecular proportion of salt	Apparent hydration value per molecular proportion of salt	Ratio of rates per molecular proportion of salt	Density t = 25°	Volume	Increase per molecular proportion of salt	K corrected for increase in volume	Increase (total)	K corrected for increase in volume of sugar solution	Increase (total)
1	0 25	50	0	607				1 07653	1076 1		607		671	
			1	569	62	4	1	1 13138	1209 8	188 7	640	133	721	150
			2	614	53 5	3 4	0 86	1 17396	1344 9	134 4	767	260	865	294
			3	651	48	2·93	0 77	1 20604	1481 1	135	896	389	1010	439
1	0 5	100	0	217				1 05631	2030 4		217		281	
			1	259	22	7 5	1	1 08904	2162 4	132	254	37	271	40
			2	254	18 5	6 2	0 84	1 11798	2294 5	132 1	287	70	306	74
			3	265	16	5 3	0 73	1 14222	2429 9	133 2	317	100	337	106
1	1	200	0	98 7				1 04494	3940 4		98 7		101 8	
			1	105 9	7 2	14	1	1 06388	4069 8	129 4	109 4	10 7	112 8	11
			2	111 1	8 2	11	0·85	1 07963	4203 3	131 4	118 5	19 8	122 2	20 4
			3	115	5 4	9 3	0 73	1 08517	4396 6	131 7	126 5	27 8	130 5	28 7

Table II—Hydrolysis of Cane Sugar by Tolueneparasulphonic Acid in presence of Potassium Tolueneparasulphonate

Water and salt constant , acid varied , sugar 0 5.

"Water" OH$_2$	Salt	Acid	K'	K' in absence of salt	Increase	
					Absolute	per cent
100	2	2	569	507	62	12 2
100	2	1	354	217	37	17 1
100	2	0 5	117·9	98 7	19 ·2	19 5

The values given under the heading " hydration value " are based on the assumption that the increase in the velocity coefficient is due to the " dehydrating " influence of the salt the behaviour of the different salts in this respect is displayed in a more striking manner in Diagram C It has often been pointed out previously that the apparent hydration value

Table III—Hydrolysis of Cane Sugar by Tolueneparasulphonic Acid in presence of Various Tolueneparasulphonates

A $100\ H_2O : 0\ 5\ C_{12}H_{22}O_{11}$

Salt	K'	Volume	Weight of salt	Apparent hydration value
Acid	217	2080 4	—	—
K	239	2162 4	210	7 5
Ca/2	243	2144 8	191 2	9 5
Sr/2	241	2145 8	214 9	8 5
Ba/2	235	2146 8	239 8	7
Zn/2	245	2142 0	203 8	10
Cd/2	244	2145 2	227 3	10
2K	254	—		12 5
Ca	264	2259 9	382 3	15 5
Sr	259	2262 4	429 9	14
Cd	274	2262 6	454 7	18
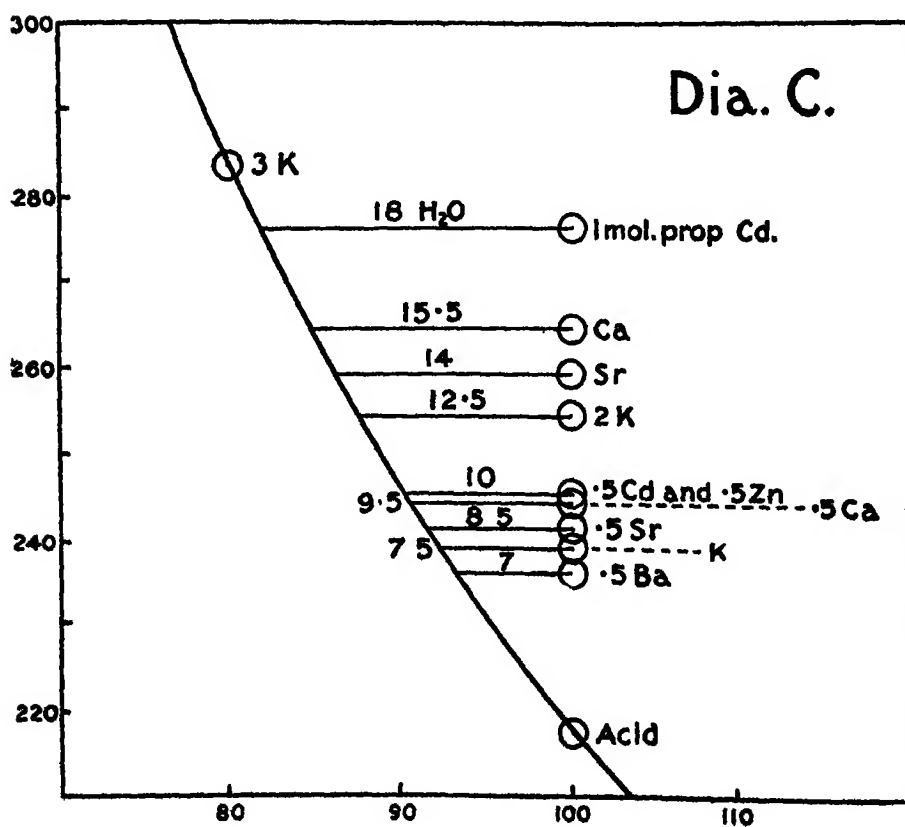
probably includes all the effects produced by the salt in the solution and is chosen merely as a convenient means of giving expression to the combined influence of these effects, not as an absolute value.

The Arrhenius hypothesis involves the conclusion that when a neutral salt is added to a solution of the corresponding acid the degree of dissociation of each compound is diminished, so that the concentration of the hydrogen ion, which is assumed to be the effective agent in the solution, should be diminished   As a matter of fact, the " molecular conductivity " of the mixture is less than the sum of the individual molecular conductivities of the two constituents   nevertheless, the hydrolytic activity of the acid in presence of the salt is greater, as a rule, than that of the acid alone   This has always been a stumbling block to those who advocate the electrolytic dissociation hypothesis as an explanation of chemical action

Latterly, the view has been put forward that both the undissociated (unionized) and the dissociated molecules are active and not only so but that the former are the more active   That this hypothesis is being treated seriously is evident from the fact that one of the most recent communications from the laboratory of the Nobel Institute, under the charge of Arrhenius, is entitled—" The catalytic activity of the undissociated molecule" (by Hugh Stott Taylor) * No definite conclusion is arrived at, however   But it is noteworthy that in an earlier communication by the same author† it is pointed out that three hypotheses have been put forward in elucidation of the phenomena under consideration—" the hydrate theory of Armstrong and his co-workers   the theory of Arrhenius in which the ions are regarded as exerting an accelerating influence on each other   and lastly, the recent suggestion by Snethlage whereby neutral salt action is explained on the assumption of catalytic activity of the undissociated molecules "   Then follows the remark, " the first hypothesis has on frequent occasions been shown to be untenable."

With regard to this last statement, we wish to be informed where and when   We are not aware that more than the most perfunctory consideration has ever been given to our evidence and arguments—Lundén,‡ indeed, has referred to some of our work but only in a most superficial manner

Whatever be the ultimate decision with regard to the hypothesis that not only the ions but also the undissociated molecule of the acid possesses specific hydrolytic activity, the admission of such a possibility by the chief advocates of the dissociation hypothesis is of deep significance.   As this hypothesis

* 'Meddel K. Vetensk. Nobelinstitut,' 2, No. 37 (1913)

† *Ibid.,* No. 34, p 19

‡ *Ibid*, Bd 2, No 3, p. 5 (1910).

loses its one distinctive feature when thus shorn of its pristine simplicity and, therefore, ceases to be of any particular value as a direct and in itself sufficient explanation of the phenomena of chemical change in solution, the claims put forward on its behalf must be abated *

Our work has involved the careful study of the hydrolytic activity of a number of strong acids as tested by means of cane sugar and of the influence of a variety of salts on the process it has also included an equally careful study of the hydrolytic activity of chlorhydric and of nitric acid towards methylic acetate and of the influence of salts of these acids   Moreover, we have sought to determine the influence of non-electrolytes such as acetic ether and various alcohols on hydrolytic changes.† We can, therefore, claim wide personal experience of the phenomena under consideration and that we have a large number of data at our disposal which have been collected with as much care as it is in our power to bestow upon the inquiry and the data are strictly comparable, as we have always used " weight normal " solutions We may here again direct attention to the impossibility, in the case of solutions which are at all concentrated, of basing conclusions on observations made with solutions of " volume-normal " strength

The preliminary experiments made with methylic acetate‡ were inconclusive however, together with the earlier observations made by Arrhenius, they afforded proof that the behaviour of this substance as a hydrolyte is altogether different from that of cane sugar   This was shown to be the case when the investigation was subsequently carried out by one of us, with all possible care, in 1912 (No XXIII)

Totally different values were obtained by the two methods , the results obtained with hydrogen chloride at different dilutions are shown in the table on p. 107

It was then pointed out that—

" There is much to show that there is an actual difference due to the character and influence of the hydrolytes. The effect of substances such as methylic acetate on other substances in solution is very different from the effect of cane sugar   The large effect that substances which have no great affinity for water, such, for instance, as propylic alcohol, with which methylic acetate may well be compared, have in reducing the solubility of salts in water would tend to show that such substances have a large effect on the condition

* F. P. Worley, " The Decline of the Hypothesis of Ionic Dissociation," ' Phil. Mag ,' 1914, p 459.

† These Studies Nos. I, III, IV, VIII, X, XII, XIV, XV, XVI, XIX, XXII, XXIII, XXIV.

‡ Armstrong and Watson, 1907, No IV.

of other substances in solution. Cane sugar has an entirely different effect and it is highly probable that the actual condition of the salts and acids is different in the presence of even small amounts of methylic acetate from what it is in the presence of cane sugar"

Molecular proportions of total water	Apparent molecular hydration values		Molecular hydrolytic activity	
	(Methylic acetate)	(Cane sugar)	(Methylic acetate)	(Cane sugar)
30	2 5	12 4	356	518
40	3 5	13 6	345	486
50	4 2	15 1	339	465
60	4 6	16 8	336	444
70	4 9	18 2	334 5	
80	5 0	18 7	334	428
90	5 0	19 2	333 5	
100	5 0	19 8	333 5	419
200	5 0	—	333 5	

The differences that we have established between the two hydrolytes have been entirely disregarded by the workers in the Nobel Institute and no attention has been paid to our work on the influence of non-electrolytes

It is clear that no attempt has been made by our critics to understand our "theory"—which, be it remarked, is not a "hydrate theory" in the ordinary sense of the term but an attempt, such as no one else has made, to provide a definite and complete explanation of the nature of the changes which attend dissolution and of the interactions which underlie the phenomena of hydrolysis in solutions generally, especially concentrated solutions.

The "theory" of Arrhenius, in which the ions (of the acid and of the salt) are regarded as exerting an accelerating influence on each other, is not only— when thus barely stated—in obvious contradiction to the terms of his own primary hypothesis of electrolytic dissociation but also one which does not appear to be in harmony with the facts. By themselves, neutral salts generally are entirely without action as hydrolytic agents and no direct interaction of an acid and its neutral salt can be imagined that will either give rise to an agent which is more active than the acid itself or confer specific hydrolytic activity upon the salt. As a matter of fact, the suggestion made by Arrhenius, in the publication cited by Taylor,[*] is of far wider import than Taylor indicates—it is that foreign substances, in general, increase *the osmotic pressure* and, therefore, accelerate change in a solution. But after all, this is no explanation and little more than a paraphrase of patent facts: one

* 'Zeit. physik. Ch.,' vol. 28, p. 399 (1899).

unknown (the cause of the acceleration) is not to be accounted for and explained by another unknown (osmotic pressure), as, two unknown causes do not constitute a known cause   But the views put forward by Arrhenius in 1889 and subsequently on the influence of salts are full of feeling and clear proof of his appreciation of the situation   divested of their ionic garb, his views probably do not differ very materially from ours.   Over and over again, this acute observer has called attention to variations in the amount of the active as distinct from the inactive part of the hydrolyte—but he has assumed that this varies concomitantly with and is conditioned by a variation in the concentration of the hydrogen ions   Taylor, however, in his recent communication dealing with various ethereal salts, comes to the conclusion that the action of neutral salts is probably independent of the hydrolyte and most followers of Arrhenius appear to have entertained this view and to have overlooked his early statements

Lundén, it may be added, quotes the fact that a salt may accelerate one set of changes (the hydrolysis of sugar and of ethereal salts by acid) whilst it may retard another set (the hydrolysis of ethereal salts by an alkali) as proof that the action of salts is not to be explained by regarding them as dehydrating agents

Our view of the matter involves the assumption that the components of a solution act reciprocally and that the interactions which take place in a solution—changes such as attend the hydrolysis of sugar or of an ethereal salt, for example—are effected within complex systems the components of which are produced by the reciprocal interaction of solvent and solute or solutes   We consider, moreover, that it is necessary also to take into account the changes which are produced in the solvent itself—more particularly when this is water

In discussing the nature of hydrolytic processes (XXIV)* we have given the scheme on p 109 as representing the hydrolysis of a sugar or of an ethereal salt

The dotted lines indicate the directions in which cleavage takes place, the double arrows those in which the affinities may be supposed to operate within the complex system

Two of the components of the system are the two substances formed by the reciprocal interaction of the potential electrolytes, hydrogen chloride and water, which thus become activated ("ionized"), but the hydrolyte is also activated by hydrolation and converted into a substance which though not an electrolyte as a whole behaves "locally" as an electrolyte and is eventually hydrolysed—because it is electrolysed locally

* 'Roy Soc Proc.,' A, vol 87, p 617 (1912)

Hydrolated hydrolyte | Hydrolyst
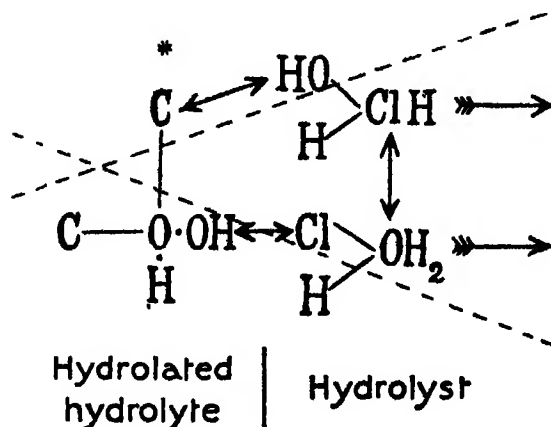
As the concentration in a solution is diminished, more hydrolated and weaker forms of the substances present come into existence   Some of these can interact more or less at a distance—in conveying an electric current, for example   But perhaps the hydrolyte must always be brought into close conjunction with the hydrolyst, and even if effective in some degree at all concentrations, it is to be supposed that the hydrolyst is more effective at some particular stage of "hydrolation" of the hydrolyte

From such a point of view, it is not difficult to understand the effect produced by a salt in altering the rate at which hydrolysis is effected   Salts cannot fail to act as "dehydrolating" agents (cp No VI), both by directly withdrawing water from the solution and by altering the state of the solvent water, the necessary consequence must be that when a salt is added to a solution the degree of hydrolation of every hydrolated constituent of the solution is lowered, and up to a certain point this change must involve an increase in the rate at which hydrolysis proceeds   In the case of strong hydrolytes, such as cane sugar, it will not be easy to pass this point, but in the case of weak hydrolytes such as the ethereal salts, probably the concentration is soon reached at which the hydrolyte has maximum efficiency and if the salt carry dehydrolation beyond this point, it will diminish instead of increasing the apparent activity of the acid

The great difference in behaviour of the two classes of hydrolyte is, doubtless in part, if not in large part, determined by the different effects they themselves produce upon the "condition" of the solution, it is to be supposed that the ethereal salts determine dissociative changes of a far reaching character in the solvent water which render this a more active dehydrolating agent, hence it is apparently that the "hydration values" deduced by using ethereal salts are

* The oxygen junction of an etheric compound is represented in this scheme.

so low and even negative in some cases   The apparent inertness of salts in presence of alkalies and the negative effect of a trichloracetate on the hydrolysis of acetic ether by trichloracetic acid observed by Taylor both meet with an explanation from this point of view.

But we have also to take into account the fact that the sugars are hydrolysed only by acids whilst the ethereal salts are more catholic in their behaviour and are equally readily hydrolysed by acids and by alkalies   In the case of the latter, the immediate neutralisation, as the action proceeds, of acid by base must be the cause of far reaching changes in the constitution of the solution, as not only is the amount of the hydrolyst and of the hydrolyte as well as of the non-electrolyte subject to constant diminution but, at the same time, a second metallic salt is introduced into the system, in place of the base, which probably affects the solution less than the base does, it may well be that these changes balance and outweigh the effect produced by a salt added purposely, so that this salt is either apparently without influence or even has a negative influence   It need scarcely be pointed out that, in making these suggestions, we are merely calling attention to the possibilities, the complexities of the problem are such that it appears to us to be impossible to place any absolute interpretation upon the facts

The activity of the acid will probably increase up to a point beyond that at which the hydrolyte loses in activity—but being the more sensitive, the hydrolyte will suffer more than the acid   When only a small proportion of acid is present relatively to the salt, the latter will have a still greater opportunity to influence the hydrolyte, on this account, it is to be expected that salts will have a relatively greater influence in presence of a minor proportion of acid—as indeed appears to be the case

There is every reason to believe that the progressive addition of small equal amounts of acid would involve, in the case of each addition, less change in the solution, whatever the nature of the general effect on the solution may be   Our experiments show, in fact, that each successive addition of salt to a dilute acid solution has less effect than its predecessor and that salt and acid act alike in exercising an apparent concentrating effect.   As this "salt effect" is greater per molecular proportion added the less salt is present, it follows that the salt effect should be greatest when least acid is present.

In fine, if we attempt to explain the phenomena of hydrolysis in terms of the doctrine of " electrolytic dissociation," we plunge into a maze of difficulties and contradictions, if, however, it be admitted that " hydrolation " (and the correlative change) is the effective cause of the activation

of potential electrolytes which attends their dissolution in water, there is no particular difficulty in placing a rational interpretation upon the facts, though the complexities of the problem are such that it is impossible to offer a complete solution

The compounds formed by the "distribution" of the two components of the electrolyte ("salt" and solute) against one another which are postulated by our *association* hypothesis are the ions postulated by the *dissociationists*; but, in addition, our view takes into account the activation of non-electrolytes and changes in the solvent · indeed, we regard both of these as necessary parts of the process of chemical change in solution and as equal in importance to and strictly correlative with the changes which are involved in the passage of the salt from the state of potential into that of actual activity as an electrolyte.

Morphological Studies of Benzene Derivatives. V.—The Correlation of Crystalline Form with Molecular Structure · a Verification of the Barlow-Pope Conception of "Valency-Volume"

By Henry E. Armstrong (F R.S), R. T. Colgate (B.Sc) and
E H Rodd (B.Sc)

The systematic crystallographic inquiry discussed in the present communication was commenced, about fifteen years ago, in the hope that it would be possible, by determining the morphological characters of a considerable number of benzene derivatives of simple constitution, to discover relationships from which definite deductions could be drawn as to the precise manner in which crystalline form is affected by particular alterations in molecular configuration—the ultimate object in view being to correlate internal structure with external form.

In planning the work, in order to determine the effect of all the possible variations of the position in the molecule of chlorine and bromine, it was decided to study, in the first instance, as many as could be procured of the di-substituted compounds of the form $C_6H_3R_1R_2.SO_2X$ containing either chlorine or bromine in place of R_1, R_2 and X.

The dichloro-, dibromo- and chlorobromobenzenes exist in three isomeric forms, ortho-, meta- and para-   each of these forms gives rise to several isomeric sulphonic acids—the para- to 4, the ortho- to 8, the meta- to 11 · moreover X in the radicle SO_2X may be either Cl or Br   the number of possible compounds in the group selected for study was therefore 46

The manner in which the position of the radicles may be varied, in such a series of compounds as that chosen, when only one halogen is present, is as follows —
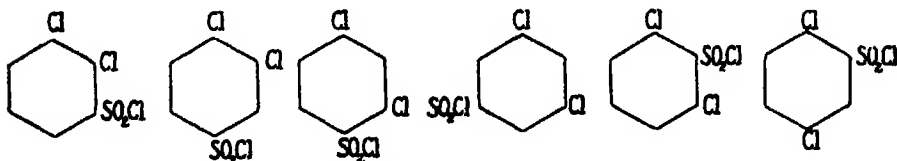
Further variation is possible, if two halogens are used   for example, in the case of the para- series—
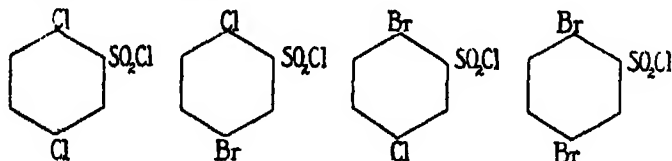
It has not yet been possible to devise methods of producing all the variants indicated but a large proportion have been prepared.   Unfortunately, however, in some cases difficulty has been experienced in obtaining crystals fit for measurement *

In the para- series, the relationships discovered are simple, as the various chloro- and bromo-compounds examined are all strictly isomorphous   later on, however, when the iodo-derivatives and more complex compounds of the sulphonamide type were examined, numerous cases of dimorphism were met with in the series.

In the meta- and ortho- series, the tendency to crystallise in several forms was apparent from the outset, particularly in the former, the 1·3:4 derivatives forming a trimorphous and the 1 3·5 a tetramorphous series.†

But although close relationships were thus established within each group

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* The fact that such difficulties are met with is in itself significant   There are, however, many deficiencies in our crystallographic technique which need to be overcome, probably, much will be accomplished in the future, by wise choice of solvent and particularly by regulating the rate of evaporation and by the discovery of temperatures at which crystallisation may be more satisfactorily effected than by allowing the growth to take place merely under atmospheric conditions

† 'Brit Assoc Rep.,' 1900, p 167 , 1902, p. 180

no direct connexion between the members of the 1 4, 1 3 and 1 2 series was discovered.

The Barlow-Pope Theory—The publication by Barlow and Pope in 1906 of their remarkable generalisation connecting crystalline form with internal molecular structure, especially in the case of derivatives of benzene, necessarily at once affected the present inquiry

The theory involves the assumption that the atoms have individual existence and are closely packed in the molecules, these latter, in turn, forming the closely packed structures which constitute the crystal

Further—and the conception is a most important and novel one—they have contended that the influence of the atoms is exercised within spheres which are approximately proportional in volume to the fundamental valencies of the atoms and that the valency volumes are *relatively* constant in all cases thus, regarding the valency volume of hydrogen as unity, that of carbon is taken as 4, that of nitrogen as 3, that of oxygen and sulphur as 2, the halogens all ranking with hydrogen as of unit volume   In this respect, the theory is entirely at variance with the views held previously that elements of the same valency differ in atomic volume, a doctrine dating back to the time of Kopp, as it involves the assumption that, whilst they retain their relative spheres of influence, the atoms alter in "volume" according to the conditions under which they are placed.

The structure of benzene arrived at by Barlow and Pope is represented in perspective in fig. 1 and in plan and elevation in figs. 2A and 2B.   It will be noticed that in fig. 2A only those atoms of carbon which are supposed to be in combination are shown as in contact   in the final arrangement in the crystal of closely packed units, the atoms are brought together, it is supposed, in the manner represented in the projection given in fig. 3 two of the atoms in the upper and also two in the lower plane, shown in plan in fig. 2A, thus become approximated and as a consequence of this distortion the symmetry of arrangement is slightly disturbed.

Fig 1.

Equivalence Parameters of Benzene.—The great advance made by Barlow and Pope in discussing crystallographic data depends on their use of equivalence parameters in place of axial ratios.   These latter represent only the relative dimensions of the structure in three directions, without reference to any unit of size · by introducing such a factor, namely the volume of the

molecular unit—the valency volume—and calculating three dimensions, proportional to the axial ratios, the product of which is equal to this valency volume, three values are obtained which represent the dimensions of the cell within which the crystal units can be closely packed   These
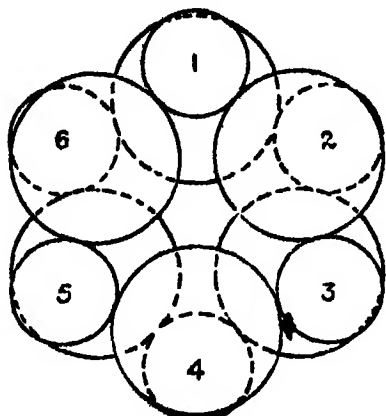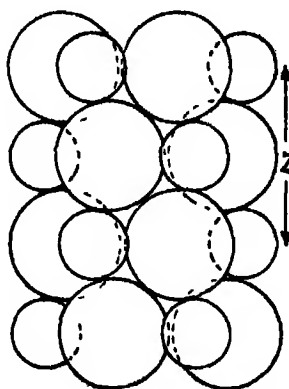
Fig 2A   Fig 2B
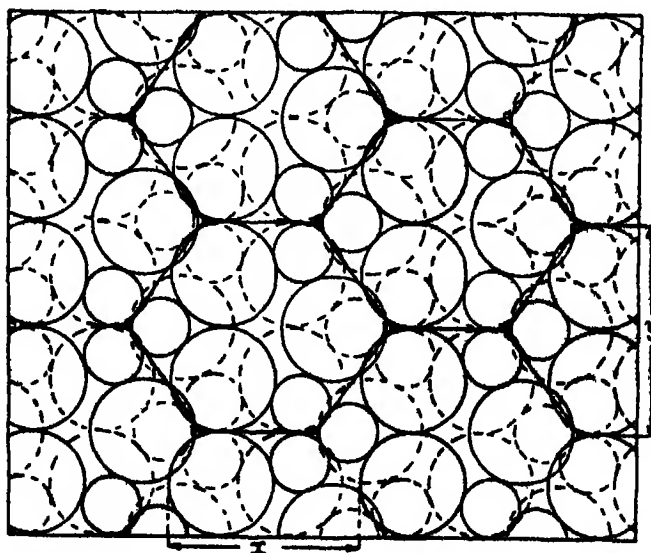
Fig 3

three dimensions, termed *equivalence parameters*, x, y and z, are calculated in the following manner from the axial ratios $a \cdot b . c$ and the valency volume W —

$$x = \sqrt[3]{\frac{a^3 W}{c \sin \beta}}, \quad y = \frac{a}{a}, \quad z = cy.$$

The equivalence parameters of orthorhombic benzene are .

$$x \ y \ z = 3{\cdot}101 \cdot 3\,480 \cdot 2\,780$$

The directions x, y, z, are indicated in figs. 2B and 3   It will be noticed that z (fig. 2B), the thickness of a single layer of benzene molecules, is rather less than the sum of the diameters of a carbon and of a hydrogen sphere, owing to the interpenetration of the layers , y, on the other hand, is equal to twice the diameter of a carbon sphere , x, the dimension at right angles to y, is of less value why this is the case will be seen on reference to fig 3, which indicates the manner of packing the several units.

Equivalence Parameters of the Derivatives of Benzene.—In their first communication in which they discussed the crystallography of quinol, resorcinol, catechol, triphenylcarbinol, triphenylacetic acid and triphenylamine, Barlow and Pope were able to show that whilst the z value remained practically constant the two other dimensions were modified in accordance with the alterations made in the structure by the radicles which were introduced. In two later communications, dealing with trinitro-derivatives of benzene, only the z value was taken into account and shown to be in fair agreement with that of orthorhombic benzene (2 78), excepting that in a few cases a lower value, approximately 2 6, was met with

Successive layers of benzene molecules may conceivably be arranged in the two different ways shown in figs 4 and 5, the one representing an ortho-
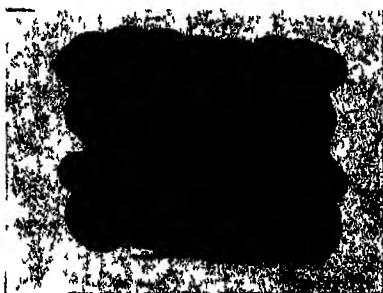
FIG. 4.   FIG. 5.

rhombic and the other a rhombohedral arrangement· in the former, the successive layers are directly superposed, molecule falling upon molecule, whilst in the latter they are so shifted laterally that each molecule in the upper layer is in contact with three molecules in the layer below In consequence of this shifting, the thickness of the layers is diminished to some slight but unknown extent. The two types of arrangement are termed by Barlow and Pope the hexagonal and the rhombohedral marshallings· it has

been supposed by them that the latter form prevails in cases in which a z value markedly lower than 2 78 is met with   Since the rhombohedral type of marshalling can be derived, in a simple manner, from a cubic closely packed arrangement of equal spheres, it is conceivable that, in derivatives possessing this marshalling, an approximation to cubic symmetry may be revealed in the crystalline form—and as a matter of fact, not a few of the compounds to be described are pseudocubic in form

In discussing the crystalline form of certain picryl derivatives, Jerusalem and Pope* in 1908 and Jerusalem† in 1909 came to the conclusion that the majority of the substances considered were of orthorhombic type (hexagonal marshalling)   in a few cases, however, on account either of the low value of the z parameter or of the pseudocubic character of the crystals, they supposed that the rhombohedral marshalling prevailed

In 1910, in the first and second of these Studies,‡ in dealing with 29 compounds of the para- series of the form $C_6H_3R_1R_2SO_2X$, the conclusion arrived at, stated in general terms, was that a " benzene framework " was traceable in all cases   This was based mainly on the occurrence either of z values corresponding to one or other of the two types of marshalling referred to above or of pseudocubic structure, but in the majority of cases, the marshalling was considered to be of rhombohedral type, mainly on account of the frequent occurrence of pseudotrigonal ratios

No definite conclusion was reached either by Jerusalem and Pope or by ourselves with regard to the significance of the x and y values that were deduced . it was clear that the increase due to the introduction of the sulphonic radicle affected mainly the x parameter but the y value bore no obvious relation to that of benzene and was conspicuously low : both x and y varied considerably in value.

At this time, no special use had been made of models and we were mainly concerned in proving a direct relationship in crystalline form between benzene and the derivatives considered.

In extending the inquiry, the experience gained in examining the various sulphonates referred to in Nos III and IV of these Studies§ has been of material assistance, as, in discussing their properties, it was found to be possible to give a rational interpretation of the crystallographic measurements in terms of the Barlow-Pope theory in complete accordance with the expectations to which chemical considerations give rise.   Perhaps the most important

* 'Roy Soc. Proc.,' A, vol. 80, p 557 (1908).
† 'Chem. Soc. Trans.,' vol 95, p. 1275 (1909)
‡ 'Chem. Soc. Trans.,' 1910, p. 1578.
§ 'Roy Soc. Proc.,' A, vol 87, p 204 (1912) , vol. 89, p. 292 (1913).

advance made at this stage was the explanation given of the manner in which water of crystallisation is included in the structure

It is noteworthy that in the case of all the salts considered (various substituted benzenesulphonates and several toluenesulphonates), excepting silver tolueneparasulphonate, the z value deduced was low (from 2 64 to 2 68, that of the silver salt alone being 2 795), on this account, it was supposed that the units were disposed in rhombohedral marshalling

The Influence on Crystalline Form of simple Radicles of the same Valency Volume as Hydrogen   Effect on the x *Parameter of the Radicle* SO$_2$Cl

We have now to consider the results obtained on further discussion of the data presented in 1910 in Parts I and II of these Studies relating to compounds of the para-series and also of numerous unpublished observations relating to the isomeric compounds of the 1 3 and 1 2 series

In the course of the work, much use has been made of solid models and we ascribe our success largely to their introduction, indeed, without such models, it is almost impossible to visualise the changes in form corresponding to known variations in chemical composition when these are of any degree of complexity.

As, by hypothesis, the atoms of the halogens occupy approximately the same volume as hydrogen atoms, in discussing the data relating to compounds of the form $C_6H_3R_1R_2 SO_2X$, it is sufficient to consider the probable structure or structures of benzenesulphochloride, $C_6H_5 SO_2Cl$

The form of structure of a unit of this substance obtained by substituting one hydrogen atom in the benzene complex by the group (SO$_2$Cl) is shown in the photograph fig. 6.   The sulphur atom takes the place of the hydrogen

Fig 6.

atom and is in contact with three carbon atoms. two oxygen atoms are
in contact and presumably combined with the sulphur atom but in a
slightly lower plane and are also each in proximity to two carbon atoms·
the sulphonic halogen atom which is in contact with both the sulphur atom
and with the carbon atom to which the latter is attached lies between the two
oxygen atoms   it is open to question whether this atom be not in connexion
with these oxygen atoms rather than with the sulphur atom.

Units of this kind, packed together in the manner shown in the diagram
fig. 7, form an assemblage of dimensions corresponding to the crystallo-
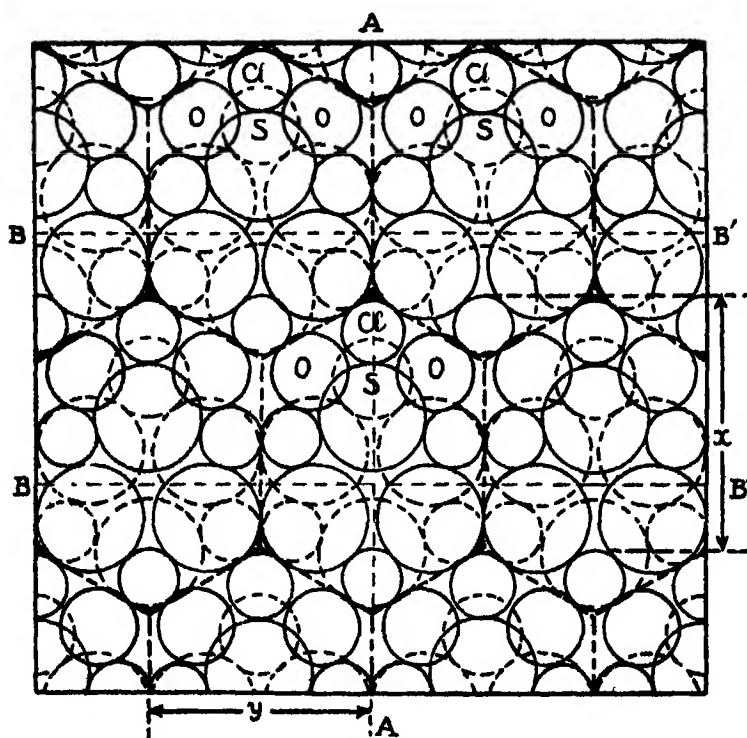
FIG 7.

graphic data of most of the substituted sulphochlorides which we have
examined

The diagram shows one layer of units in plan, the dotted and full line
circles being the projections respectively of the lower and of the upper layers
of spheres comprised in the units.

The units are all similarly directed and the structure is very closely related
to that of benzene ; it may be regarded as derived from that of benzene (fig. 3)
by the removal of one hydrogen sphere from the corresponding position in each

benzene unit and the introduction of the group (SO_2Cl) into its place. The result of this displacement is to open out the structure in the direction of x

Successive layers are packed so that the centres of units lie vertically over one another (*i.e.* in hexagonal marshalling) but in alternate layers each unit is rotated through 180° about an axis represented as BB' in the diagram. this then becomes a digonal axis of symmetry · the symmetry of the structure is therefore monosymmetric.

The diagram is drawn from a model of the assemblage and the radii of the spheres are made proportional to the cube roots of the valency volumes of the atoms they represent Assuming that the dimension of the structure perpendicular to the plane of the paper is the same as that of benzene, *i e* 2 780, the translations in the directions of the edges of the drawing marked x and y are found to be 3 82   3·38   These figures agree remarkably well with the equivalence parameters of paradibromobenzenesulphochloride This compound crystallises in the monosymmetric system, $a : b \; c =$

2 476 · 1   1 144. $\beta = 95° \; 26'$, taking $a/3$ and interchanging a and c, the equivalence parameters become $x \quad y \quad z =$ 3·856   3 371 . 2·782, the agreement is rendered even closer if allowance be made for the slight distortion which has changed the angle β from 90° to 95° 26', as $3·856 \times \sin 95° \; 26' = 3·838$ The structure depicted is therefore in complete accordance with that of the actual crystal.

Fig 8

The photograph (fig. 8) gives a good idea of the appearance of a structure composed of models of benzenesulphochloride packed together in the manner described.

The values thus found in the case of dibromobenzenesulphochloride are in marked contrast with those deduced previously, viz —

	x	y	z
Former values ..	5 787 .	2 337 .	2·674
Present values ...	3·856 .	3 371	2·782

The difference is due to the fact that formerly the dimensions of the x and y parameters were not specially considered and that, in recalculating these parameters, the axial ratio $a : b$ has been divided by 3, this factor being that found *by trial* to give values in accordance with the projection of the model of the crystalline structure.   In consequence of this change, the z

value is transferred from the c to the a axis—hence the alteration in this value also

Applying the method in the manner explained to the data in our possession for 31 compounds of the type $C_6H_3R_1R_2SO_2X$, we obtain the results embodied in Table I, which includes 14 examples of disubstituted sulphochlorides and bromides of the para-series 6 of the meta- and 8 of the ortho-series, together with 3 monosubstituted sulphochlorides, all being of one valency volume—36

The mean values are as follows —

$$
\begin{array}{ccc}
x & y & z \\
3\cdot904 & 3\ 360 & 2\ 772
\end{array}
$$

the extremes being

$$
\begin{array}{ccc}
3\ 806 & 3\ 222 & 2\ 680 \\
4\ 040 & 3\ 419 & 2\ 865
\end{array}
$$

The values assigned by Barlow and Pope to benzene itself are

$$
\begin{array}{ccc}
3\ 101 & 3\ 480 & 2\ 780
\end{array}
$$

It may be noted that these are deduced from observations which, it is probable, are open to improvement

The results thus arrived at are not only remarkable by reason of the proof they afford of a definite relationship between all the various simple sulphonic derivatives considered but especially as a verification of the Barlow-Pope generalisation

Taking into account the fact that the position occupied by chlorine, bromine and iodine in the molecule has been varied almost in every possible way, the proof obtained that these elements and hydrogen have the same relative valency volume is little short of absolute

Attention may also be directed to the fact that not only is the z value that of benzene but, in all cases, that which corresponds to the orthorhombic arrangement or hexagonal form of marshalling

The y value, in like manner, is in agreement with that of the benzene itself.

With regard to the third or x parameter, the one direction in which, presumably, an elongation of the structure is effected by the addition of the SO_2Cl complex, the difference between the x value of benzene and that found, $3\ 904 - 3\ 101 = 0\ 803$, may be regarded as the value of the increment due to the introduction of the group $SO_2Cl(Br)$ in place of an atom of hydrogen   The value deduced from the projection is $0\ 78$

At this point, advantage may be taken of the opportunity to justify the method adopted in arriving at the above important series of conclusions, as it is one that involves a modification of the observed axial ratios in the manner

Table I

	Orientation					a	b	c	β	Fractions used	x	y	z
	1	2	3	4	5								
1	SO₂Cl	Cl	—	—	Cl	2·450	1	1·179	97° 25'	$a/3$	3·954	3·353	2·788
2	SO₂Br	Cl	—	—	Cl	2·490	1	1·166	98 41	$a/3$	3·907	3·351	2·781
3	SO₂Cl	Cl	—	—	Br	2·509	1	1·178	97 40	$a/3$	3·921	3·328	2·784
4	SO₂Br	Cl	—	—	Br	3·631	1	1·171	98 35	$a/3$	3·897	3·328	2·807
5	SO₂Cl	Br	—	—	Cl	2·398	1	1·183	98 5	$a/3$	3·874	3·419	2·733
6	SO₂Br	Br	—	—	Cl	2·488	1	1·145	97 45	$a/3$	3·885	3·393	2·757
7	SO₂Cl	Br	—	—	Br	2·476	1	1·144	95 26	$a 3$	3·856	3·371	2·782
8	SO₂Br	Br	—	—	Cl	2·479	1	1·145	96 49	$a/3$	3·860	3·371	2·786
9	SO₂Cl	I	—	—	I	2·489	1	1·154	95 50	$a/3$	3·883	3·365	2·769
10	SO₂Cl	Cl	—	—	I	2·583	1	1·176	99 7	a,d	3·883	3·302	2·843
11	SO₂Br	Br	—	—	I	2·567	1	1·167	100 30	$a/3$	3·877	3·222	2·843
12	SO₂Cl	I	—	—	Br	2·555	1	1·158	94 23	$a/3$	3·845	3·321	2·828
13	SO₂Cl	I	—	—	I	0·815	1	0·673	95 28	—	4·040	3·291	2·719
14	SO₂Cl	Cl	—	—		0·851	1	0·673	95 46	$2c$	3·984	3·389	2·680
15	SO₂Cl	Cl	—	Cl		0·834	1	0·570	97 14	$2c$	3·838	3·367	2·808
16	SO₂Cl	Br	—	Br		0·685	1	0·563	97 27	$2c$	3·806	3·380	2·823
17	SO₂Cl	Cl	—	Br		0·818	1	0·575	90 0	$2c$	3·875	3·370	2·757
18	SO₂Br	Br	—	Cl		0·818	1	0·568	90 0	$2c$	3·852	3·391	2·757
19	SO₂Cl	Br	—	Cl		0·7997	1	0·563	90 0	$2c$	3·850	3·419	2·734
20	SO₂Cl	—	Cl	Cl		1·683	1	1·154	105 2	$a/2$	3·932	3·407	2·783
21	SO₂Br	—	Br	Cl		1·600	1	1·139	106 9	$a,2$	3·932	3·452	2·762
22	SO₂Br	—	Br	Br		1·601	1	1·141	105 29	$2a/3, 2c$	3·931	3·445	2·758
23	SO₂Cl	—	Br	Cl		1·293	1	0·585	102 30	$2a/3, 2c$	3·863	3·319	2·861
24	SO₂Cl	—	I	Br		1·282	1	0·576	104 0	$4a/3$	3·862	3·363	2·865
25	SO₂Cl	—	I	Cl		1·0294	1	1·176	94 31	$a/3$	3·867	3·304	2·817
26	SO₂Cl	—	I	I		2·886	1	1·164	94 39	$a/3$	3·948	3·392	2·697
27	SO₂Cl	—	I	I		2·888	1	1·166	94 18	$c/3$	3·951	3·388	2·697
28	SO₂Cl	—	I	Cl		0·840	1	2·079	96 29	$c/3$	3·863	3·331	2·746
29	SO₂Cl	—	—	Br		0·820	1	2·074	96 47	$c/3$	3·899	3·279	2·765
30	SO₂Cl	—	—	I		0·889	1	2·074	95 22	$c/3$	3·865	3·327	2·741
31	SO₂Cl	Br	—	—		2·169	1	1·901	78 19	$3b/2$	3·929	3·443	2·717

(8) Br

shown in the column "Fractions used" and it may well be asked "if such a series of compounds as those under discussion are simply related and similar in structure, why is the similarity not at once apparent in the axial ratios as it is in an obviously isomorphous series ? "

The fact that the axial ratios may be reduced to those of one form—that of Nos 13 and 14, from which the parameters have been deduced without modification—is in itself proof of the close relationship in which the various compounds stand.

It is a well-known fact that slight changes in the conditions under which it is deposited will sometimes determine profound alterations in the external habit of a crystalline substance. The development of different sets of planes in the structure as bounding surfaces or faces of the crystal always involves such variations in habit and on account of these variations or even because they look at it merely from a different point of view, different observers often assign different axial ratios to one and the same crystal There is, however, always a simple numerical relationship between the different sets of constants so derived

The following explanation may serve to make this more evident.

In fig 9 let OA and OB be the directions of the axes a and b of a crystal and let each small rectangle represent the elevation of one side of a parallelepipedal cell, the lengths Oa, Ob being proportional to the parameters x and y The straight lines BA, BA' then represent important planes in
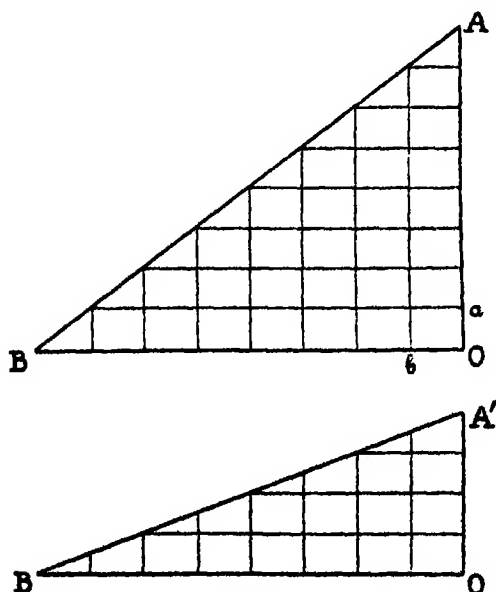
Fig. 9.

the structure which may develop as faces of the crystal. If the plane AB were developed, the observer would give the ratio $a \cdot b = OA \cdot OB$, but if A'B were developed, then the ratio $a \cdot b$ would be given as $OA' : OB$, which is but half as great as the former ratio In a similar manner, other planes might develop as faces and other values would then be assigned to the ratio $a \cdot b$

As mere changes in conditions of crystallisation can thus affect the habit of a crystal, it is more than probable that the introduction of halogen atoms into different positions in the benzene unit will also modify the crystalline habit. Such being the case, it is to be expected that the axial ratios of the members of one isomorphous series would differ from those of the members of another series much as they are seen to do in the table, all being reducible to a common form, however, by multiplication or division by some simple whole number.

The method introduced by Barlow and Pope is, in effect, one which makes it possible to recognise and allow for such departures as have been referred to, so that ultimately proper axial ratios can be deduced in cases in which the compounds examined are directly related, though not always obviously

As all the compounds included in the table can be referred to axial ratios of a similar character, it is clear that their structures can all be partitioned by three sets of parallel planes into parallelepipedal cells of similar shape · these cells, however, cannot always be of the same absolute volume, as the introduction of halogen atoms into the molecule is known to change the molecular volume. It is to be supposed that such substitutions affect each sphere of influence uniformly, so that the relative volumes of the atoms remain the same · the equivalence parameters remaining unchanged because, whilst the cell undergoes enlargement, the value of the unit valency-volume in terms of which measurement is made is correspondingly increased.

The Influence of Compound Radicles of like Valency Volume (7), SO_2Cl, NO_2, CH_3, CN, *on the* x *Parameter.*

In the previous section it is shown that the introduction of an atom of chlorine, bromine or iodine, in place of an atom of hydrogen has but a slight effect on the values of the three equivalence parameters and that the x parameter is elongated from 3 101 to $3\cdot904 = 0\,803$ by the introduction of the group SO_2Cl in place of an atom of hydrogen, we have now to consider the effect produced by other radicles of like valency-volume (7), viz. NO_2, CH_3, CN, on this parameter.

Nitro-derivatives —In the case of the nitro-compounds, the argument is the same as that adopted in the previous section but the material at disposal is limited to the isomorphous metachloro- and bromonitrobenzenes and 3 5

dibromonitrobenzene. The dinitrobenzenes crystallise in forms which cannot at present be interpreted *

The parameter values are in close agreement with those deduced from the sulphonic derivatives, the value of the increment on the x parameter due to the introduction of the group NO_2 falling well within the limits observed in that series, 0 705—0 939

m-Bromonitrobenzene is described by Bodewig† as orthorhombic, a b $c =$ 0 4957 1 · 0 5549. The same observer has described 3 5-dibromonitrobenzene as monosymmetric, a $b : c =$ 0 5795 1 : 0 2839, $\beta = 56° 12'$ Changing {001} to {101} in this latter compound and multiplying c by 2, the axial ratios become a $b \cdot c =$ 0 4836 1 0 5675, $\beta = 94° 35'$ a close morphological relationship is thus revealed between the mono- and dibromo- derivatives On calculating the equivalence parameters for these compounds, taking $2c/5$, the values obtained are those given in the following table, including m-chloronitrobenzene, which is isomorphous with the bromo-compound $(a$ b $c =$ 0 4975 1 0·5608)

	x	y	z
Metachloronitrobenzene	3 8462	3 4119	2 7433
Metabromonitrobenzene .	3 8238	3 4157	2 7564
3 5-Dibromonitrobenzene .	3 9190	3 3379	2·7609
Means .. .	3 8630	3·3885	2 7535

Methyl-derivatives.—Tolueneparasulphonic-chloride unfortunately crystallises in the anorthic system but paranitrotoluene‡ is orthorhombic, a b $c =$ 0·9074 : 1 : 1 0965 Taking $3b/2$, the valency volume being 42, the parameters are found to be —

	x :	y	z
Paranitrotoluene	4 5622	3·3350	2·7597

It is clear, on comparing these parameters with those given above, that the introduction of the methyl group into the para-position produces an extension of the structure only in the direction of x, as is to be expected. The elongation produced by the group can be calculated as $(4 5622 - 3·101)/2 =$ 0·730, a value in close correspondence with the extension produced by SO_2Cl and NO_2.

Another compound which may be considered is paraxylylene bromide, $C_6H_4(CH_2Br)_2$, which crystallises in the monosymmetric system§

a	b	c			x .	y .	z
2·3262 · 1	1·6851		$\beta = 81° 4'$	$3b/2$	4 333	3 5115	2·7942

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* Bodewig, 'Jahresb.,' 1876, p. 375
† 'Zeit. Kryst Min,' vol 1, p. 587.
‡ Bodewig, 'Zeit. Kryst Min,' vol. 3, p 381
§ Muthmann, 'Zeit. Kryst. Min.,' vol. 15, p 396.

It will be noticed that the x value is slightly less and the z value slightly greater than are the corresponding values of paranitrotoluene.

Benzeneparadisulphonic-derivatives—If in the diagram of benzenesulphochloride (fig 7), we suppose the hydrogen atom in the para-position to the sulphochloride group to be displaced by a second such group, a structure is obtained corresponding to benzeneparadisulphochloride. If the original axial directions be preserved in this derived structure, it can be seen that the result of the substitution will be to extend still more the translation x, the y direction being practically unaffected   The equivalence parameters of benzeneparadisulphochloride $(x \ y \ z = 4 4082 . 3 6033 \ 2 7516)$ are in substantial agreement with this conclusion   The extension produced by the two SO_2Cl groups $(4\cdot408 - 3 101 = 2 \times 0 650)$ is slightly less than double the effect of a single such group

Both benzeneparadisulphochloride and the corresponding bromide are dimorphous and probably isodimorphous, although the stable forms of the two do not correspond crystallographically. The disulphobromide is orthorhombic (the disulphochloride being monosymmetric) the equivalence parameters are $x \ y \ z = 4 4706 \ 3 4326 \cdot 2 7370$ There is a very close resemblance between the two sets of parameters   The cause of the dimorphism will be considered at a later stage

Paracyanobenzenesulphochloride—This compound crystallises in the orthorhombic system $a \ b \ c = 1 139 \ 1 \ 1 709$ (Mummery) Taking $3b/2$, the equivalence parameters, $x \ y \ z = 4 156 \ 3 649 \ 2 770$, are obtained These parameters are very similar to those of orthorhombic benzeneparadisulphobromide the cyanosulphochloride thus affords another case of the substitution of one group for another of equal valency volume producing but a slight modification of crystal structure.

The Influence of Complex Radicles relatively in Ortho- and Meta-positions on the x *and* y *Parameters*—In the case of di-derivatives other than those of the para-series, it is to be expected that both the x and y dimensions will differ to a not inconsiderable extent from those of benzene and that the z value alone will vary within narrow limits.

Benzeneorthodisulphochloride may be taken as illustrative of the changes effected by the introduction of two complex radicles in the ortho-position.

This compound crystallises in the monosymmetric system, $a \cdot b \ c = 1\cdot5066 : 1 \cdot 0 9061$, $\beta = 90° 6'$. but it is obvious from the magnitude of β and from the general character of the crystals (*cf.* fig 27, p 158) that the symmetry of the structure is but slightly distorted from orthorhombic.

By removing two hydrogen spheres in the ortho-position from the benzene

model and introducing into their place two (SO$_2$Cl) groups, a model is obtained of which fig 10 is a photograph, Models of this kind can be packed together in a plane layer after the manner shown in the diagram, fig. 11. All the units in this assemblage are similarly orientated   the units in adjacent horizontal rows, however, are not identical but enantiomorphous   Successive layers of the structure are identical, the benzene units being stacked one upon the other according to the hexagonal type of marshalling   The structure possesses orthorhombic symmetry, having a digonal axis at BB' and digonal screw axes at AA' emerging perpendicularly from the paper at points marked C   It is easy to conceive that some slight distortion during the process of adjustment to bring about closer packing would lower the symmetry from orthorhombic to monosymmetric

Taking $a/2$, $2c/3$,   the   equivalence   parameters   are x y $z =$ 3·4046 · 4 5183 · 2 730 ·   these numbers are in close agreement with the

Fig 10
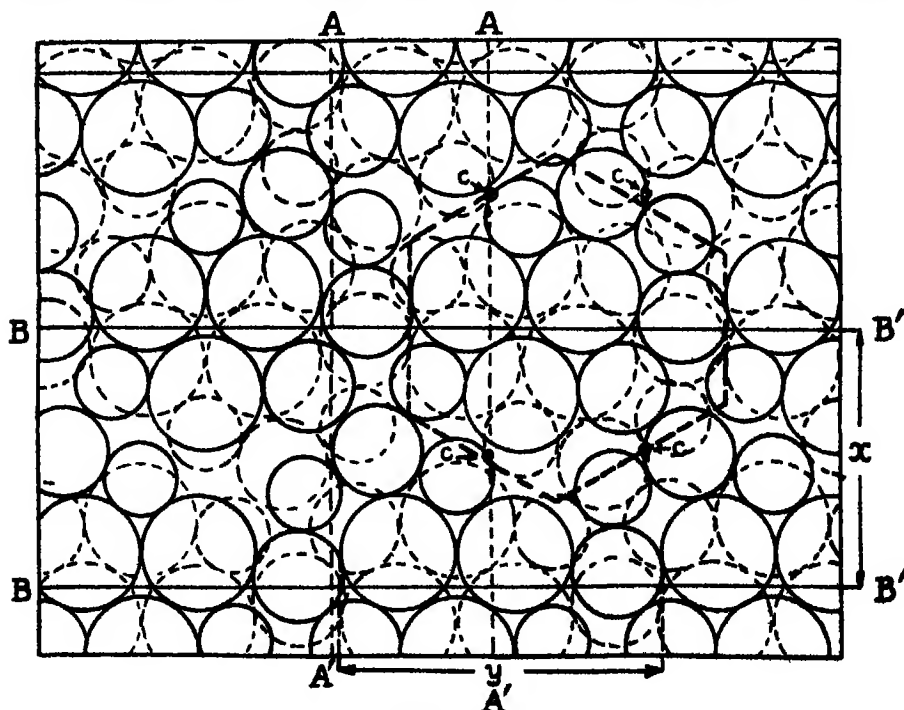
Fig. 11.

dimensions of the unadjusted structure of the diagram which are
3·47 : 4·44 : 2·73

Orthoxylylene bromide, $C_6H_4(CH_2Br)_2$ —The constants of this compound are
as follows —*

a	b	c			x	:	y	:	z
0·8591	1	0·5021	$\beta = 90°\ 0'$	3c	3·1899	·	4·6049	:	2·7404

Orthodinitroparabromobenzene, $C_6H_3Br(NO_2)_2$ —The following are the
constants of this substance —†

a	b	c		x	y	z
0·6880	1	0·5495	$\beta = 86°\ 3\frac{1}{2}'$	3·3100	4·8110	2·6436

In both these cases, the x and y values are near to those observed in the
case of the disulphochloride, so that it is evident that the effects produced
-by radicles so different as CH_2Br, NO_2 and SO_2Cl are again very similar

Meta-derivatives. Benzenemetadisulphochloride —An examination of a
structure derived from orthorhombic benzene by the substitution of two
hydrogen atoms in the meta-position by sulphonic radicles reveals the fact
that such a substitution would involve substantial increase in the y
translation and a smaller elongation of x, much as in the case of the
corresponding ortho-diderivatives The equivalence parameters of benzene-
metadisulphochloride are in agreement with this conclusion —

SO_2Cl ⬡ SO_2Cl	W		x	·	y	:	z
	42		3·2226		4·7516		2·7493

Benzenemetadisulphonamide, $C_6H_4(SO_2NH_2)_2$ —This compound may be
referred to here as one of the rare cases in which the amide occurs in a
measureable form and is neither pseudocubic nor pseudotetragonal It will
be obvious that the increase in the x and y values is such as may be
expected from the increase in the valency volume from 42 in the chloride
to 50 :—

a	b	. c			x	y	z
2·5086	1	0·9787	$\beta = 90°\ 0'$	a/2, 2c	3·4252	5·3452	2·7308

Metanitrobenzenesulphochloride —If the equivalence parameters of this
compound be calculated from the axial ratios a b $c = 1·1989$ 1 · 0·4269,
$\beta = 89°\ 23'$, taking 4c, we get $x : y$ $z = 3·2811$ · 4·6775 : 2·7368. These
are practically identical with those of benzenemetadisulphochloride : more-
over, both compounds are monosymmetric, the interaxial angle β being
very close to 90° : in each case, the direction of the parameter correspond-
ing to the thickness of one layer of benzene units is that of the axis of

* Muthmann, 'Zeit. Kryst. Min,' vol. 15, p. 396.
† 'Zeit. Kryst. Min,' vol. 1, p. 587

symmetry   It is clear, therefore, that in the case of meta-compounds, the substitution of the group (SO_2Cl) by the group (NO_2) of equal valency volume involves very little change in form

Taking the whole of the evidence brought forward in this section into consideration, it appears that whilst in the case of para-di-derivatives the alteration is practically confined to one principal direction in the crystal structure corresponding to that of the para-positions in benzene, in the case of ortho- and meta-derivatives two directions are affected

In these more complex derivatives, as in the case of those considered in the previous section, the z parameter varies only within very narrow limits.

Complex radicles such as SO_2Cl, NO_2, CH_3 and CH_2Br, which are *ex hypothesi* of equal valency volume, have practically equal influence on crystalline structure, though it is clear, as shown particularly in the case of paracyanobenzenesulphochloride, that elements of different valency volume—as is only to be expected—do not produce quite the same effect, the radicle CN, consisting of two large atoms, not "packing" quite in the same way as one made up of a larger number of smaller atoms such as SO_2Cl

It appears to us, however, beyond question that the evidence afforded by both types of compound—those containing simple and those containing complex radicles—is entirely in favour of the fundamental conception of the theory advanced by Barlow and Pope of the part played by valency volume

Influence of Three or more Complex Radicles

In discussing the data relating to trinitro- (picryl) derivatives of benzene in 1908, Jerusalem and Pope were mainly concerned in showing that "the z dimension of benzene could be distinctly traced throughout the series", the value they obtained varied from 2 699 to 2 873   Although they recognised that expansion took place in the directions x and y, like ourselves they made no particular effort to discover the laws underlying the changes. In view of the success that we have met with in dealing with the di-derivatives, we have reconsidered their data and with the aid of models and geometrical projections have deduced values which appear to be rational

In order to get a better idea of the probable dimensions of the equivalence parameters of the trinitro-derivatives, a structure was devised to represent trinitrobenzene, using spheres of appropriate sizes.   It was found that units of benzene in which the hydrogen spheres of one layer, i.e. the 1:3:5 positions, had been displaced by a nitrogen atom, could be packed together symmetrically in a plane in such manner that room was just left for the

requisite number of oxygen spheres, in groups of three, to be placed in the hollows that were left. The resulting structure had trigonal or nearly trigonal symmetry and its dimensions, supposing the z or vertical dimension to be practically that of benzene, were x y $z = 3.88$ 4.46 2.78

In Table II on p 130 are given the equivalence parameters of trinitrobenzene and picryl chloride it can be seen that these agree very closely with those of the ideal structure They differ considerably, however, from the figures given by Jerusalem and Pope, which are not compatible with this structure The table also contains the equivalence parameters of other trinitro-compounds · the values arrived at appear to be consistent with the derivation of the corresponding crystal structures from that of trinitrobenzene It will be seen that within narrow limits the z value is always that of the "benzene thickness" Attention may be directed to the striking agreement in form of 1 3 5 trinitromethylbenzene and nitromesitylene [1 3·5 trimethylnitrobenzene]

Styphnic Acid —This compound, which crystallises in the hexagonal system, a $c = 1$ 1.3890, was referred by Jerusalem and Pope to a system of orthorhombic axes, a b $c = 1.7321$ 1 1.3890, whence x y $z = 4.825$. 2.786 3.869 The y value is here the z value of benzene If styphnic acid be related in form to benzene in the way we suppose, a trigonal axis is to be looked for in the direction of the z parameter and consequently the "thickness" value should correspond to c, not to b If in the above hexagonal ratio, we halve c and throw the ratio into the orthorhombic form—

$$0.866 \quad 1 \quad (c/2)\cos 30° = 0.866 \quad 1 \quad 0.6014$$

the equivalence parameters become (W = 52)
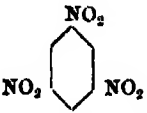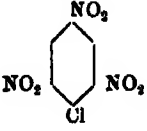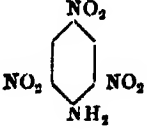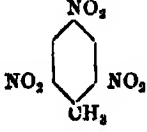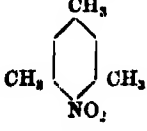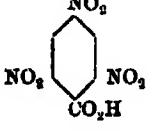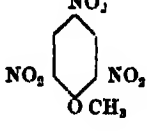
$$x \quad y \quad z = 4.0175 \quad 4.6391 \quad 2.7901$$

The figures given for trinitrophloroglucinol hydrate need similar reconsideration. This substance also is hexagonal, a $c = 1$ 1.0346 taking $2c/3$, this becomes in the orthorhombic form—$a \cdot b \cdot c = 0.8660$ 1 . 0.5973, whence x $y:z = 4.1760$ 4.8221 2.8802 The parameters thus deduced appear to be more nearly rational than those previously arrived at.

The Structure of Benzenesulphanilide and its Derivatives.
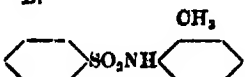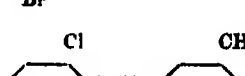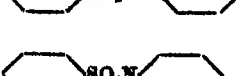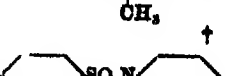
The sulphonamides do not, as a rule, crystallise in well defined forms and in the few cases in which satisfactory measurements have been secured, they have been found to crystallise in pseudotetragonal forms (Table IV, p. 143) which cannot be interpreted. The sulphanilides and similar compounds, however, usually crystallise with facility in forms well suited for measure-

Table II.

	a	b	c	β		W	Fractions used	x	y	z
(structure: benzene, NO_2 top, NO_2 left, NO_2 right)	0 9540	1	0 7330	90°	0′	48	5a/4	3 8013	4 5319	2 7868
(structure: NO_2 top, NO_2 left, NO_2 right, Cl bottom)	1 7875	1	1 2175	90	4	48	2b	3 9785	4 4520	2 7161
(structure: NO_2 top, NO_2 left, NO_2 right, NH_2 bottom)	0 838	1	0 6638	80	11	52	4a/3	4 1439	4 6297	2 7807
(structure: NO_2 top, NO_2 left, NO_2 right, CH_3 bottom)	0 9873	1	0 6724	90	0	54	4a/3	4 0055	5 0055	2 6988
(structure: CH_3 top, CH_3 left, CH_3 right, NO_2 bottom)	0 5600	1	0 4878	90	0	54	b/3	4 0984	4 7050 : 2 8004	
(structure: NO_2 top, NO_2 left, NO_2 right, CO_2H bottom)	1 7497	1 : 1 5346		90	0	56	—	4 224 : 4 816		2 758
(structure: NO_2 top, NO_2 left, NO_2 right, OCH_3 bottom)	1 7225	1 : 1 4635		91	59	56	—	4 115	4 843	2 811

ment   Having accumulated a large number of data relating to such compounds, notwithstanding the complexity of the problem, we have attempted to decipher their structure, making use of graphic methods The results arrived at are such that we venture to think our attempt is justified   The complex nature of the material discussed will be obvious on reference to Table III

Table III —Derivatives of Benzenesulphanilide

	a	b	c	β		W	Fractions used	x	y	z
Br / SO₂NH / Br (structure)	1 372	1	1 163	97°	50′	68	2a	3 234 : 7	631	2 781
SO₂NH—CH₃ (structure)	0 778	1	0 591	90	0	74	3a, 4c/3	3 427	7 999 : 2	700
Cl / CH₃* SO₂NH / Br	0 7275	1 · 1	1953	102	5	74	4a	3 3368 : 8 1238	2 7917	
Cl / CH₃* SO₂NH / Br	0 7576	1	1 1546	100	37	74	4a	3 2114	8 4287	2 7815
SO₂NH—CH₃	1 5028	1 : 1	8269	96	3	74	2a, 2c/3	3 3240	8 2028 : 2 7293	
CH₃ / SO₂NH / CH₃	0 7857	1	1 3484	97	25	80	4a	3 ·6802	8 0318	2 ·7293
CH₃ / SO₂NH / CH₃	1 7644	1	1 2344	101	56	80	3a/2, 2c/3	3 3485	8 8622	2 ·7555
CH₃—SO₂NH	1 5424	1	0 ·8980	99	11	74	2a, 4c/3	3 2660 : 8 4145	2 7277	
CH₃—SO₂NH / CH₃	0 7725 : 1	0 9494		90	0	80	4a, 4c/3	3 4406	8 4733	2 7440
SO₂N / CH₃	2 6940	1	1 ·9302	100	15	74	2c/3	3 5888	7 5134	2 7890
† CH₃—SO₂N / CH₃	2 4173 : 1 : 1 ·1363			87	6	80	a/3, 2c	3 5287	8 0074	2 8392
									Mean	2 7607

* 'Chem. Soc Journ Trans,' vol 97, p 1590 (these Studies, Part II)

† Brugnatelli, 'Zeit. Kryst Min.,' vol 30, p 191

Table III—*continued*

	a	b	c	β	W	Fractions used	x	y	z
SO₂NHPh◇SO₂NHPh	0 4645	1	0 1935	93° 41½'	106	a/2	3·054	18 151	2·545
SO₂NHPh◇SO₂NHPh	0 4973	1	0 7713	93 36	106	a/2, c/4	3 239	18 035	2 515

As benzenesulphanilide crystallises in the tetragonal system, it is not immediately comparable with the simple benzene derivatives thus far considered   Paradibromobenzenesulphanilide, however, is dimorphous   one form is nearly tetragonal and probably therefore is related closely to tetragonal benzenesulphanilide , the other—a labile form—is closely related to orthorhombic benzene   The axial ratios of the latter form are a b c = 1 372 1 1 163, $\beta = 97° 50'$ If a be doubled, W being 68, the equivalence parameters become x y z = 3 234 7 631 2 781

A structure corresponding in symmetry and dimensions to this crystalline form of paradibromobenzenesulphanilide can be built up as follows   Two undistorted benzene models are placed side by side so that two pairs of carbon and two pairs of hydrogen spheres are in contact , two hydrogen spheres in contact are then removed and two spheres of volumes 2 and 3 are substituted for them, representing sulphur and nitrogen respectively

Fig 12

This substitution causes a separation of the two benzene units which were formerly in contact, leaving room for the insertion of one oxygen atom between them   The positions taken up by the remaining atoms of oxygen and hydrogen can be seen from the photograph, fig 12, which represents a model of a single unit of the composition—$C_6H_5.SO_2NH C_6H_5$.   It should be noted that two such models can be constructed which are enantiomorphously related to one another.

Such units can be arranged in a plane layer to form a very compact structure in the manner shown in fig 13, in which the outline of each unit is defined by a broken line   Units of successive rows are in opposite orientation , digonal axes emerge perpendicularly from the points marked O

in the diagram and from all points similar to these   There are two methods of stacking these layers, one being to rotate a layer similar to the first 180° about an axis parallel to the direction of y and then to stack the units so that centres of benzene units lie vertically over one another   in the alternative method, the units of the second layer are the mirror images of those of the first, the stacking in this case also being such that the benzene units lie directly over one another   This latter is more likely to correspond with the crystal structure, as it is an internally compensated arrangement and is in accordance with the fact that hemihedral crystals of compounds of
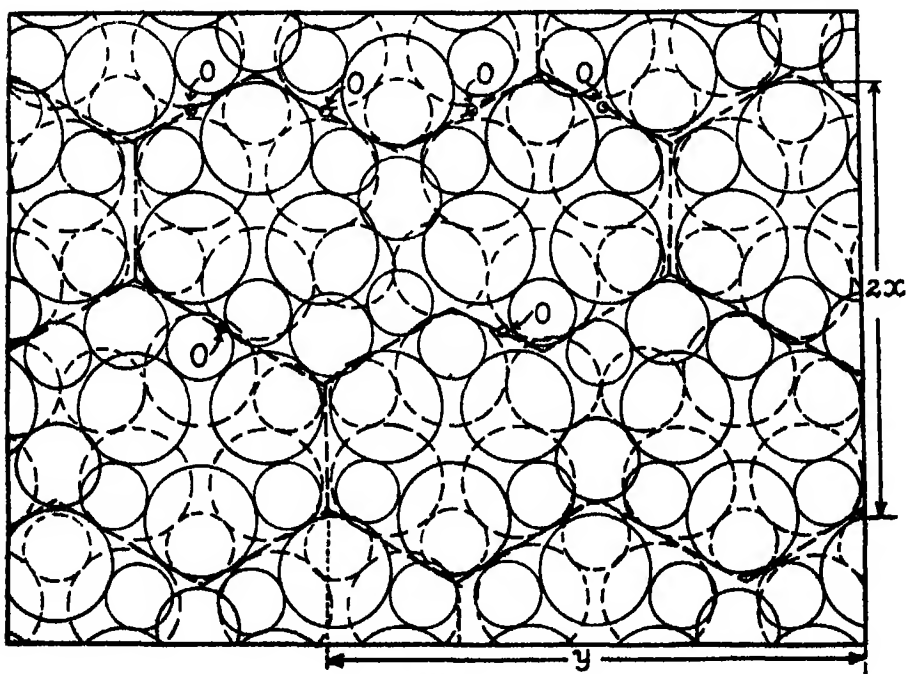
Fig 13.

this type are never observed. If one crystal only contained molecules of the one type, presumably other crystals would be formed consisting of molecules of the other type . it is to be supposed that crystals thus constituted would show hemihedral forms but such forms are not observed

No attempt is here made to explain the slight adjustments this structure must undergo to bring it into the most closely packed condition: such adjustments would involve but small changes in the dimensions of the structure and it will serve no useful end to attempt to discuss their nature. The translations of the assemblage in the directions parallel to the edges of the diagram are shown as $2x$ and y. Assuming that the vertical translation

is 2 781, the z value for paradibromobenzenesulphanilide, the other dimensions of the diagram are found to be $x \cdot y = 3\,18 \cdot 7\cdot70$ These correspond remarkably well with the parameters deduced from the measurements made of paradibromobenzenesulphanilide, viz, 3 234 · 7 631   In addition, the symmetry of the suggested structure corresponds with that observed in the case of this sulphanilide.

Benzenesulphonorthotoluidide.—If the unit of benzenesulphanilide outlined in fig. 13 be examined, it will be seen that the two hydrogen atoms in ortho-positions to the nitrogen atom are not equivalent and that therefore two different structures might be obtained by substituting the methyl group for the one or the other of these hydrogen atoms.   This does not imply that *isomeric* benzenesulphonorthotoluidides are possible, because by the simple process of altering the position of the two constituent groups of the toluidide, by rolling the sulphur and nitrogen atoms round each other in the plane of the layer, the two kinds of molecule are converted the one into the other   In the free state, the molecule probably takes up an intermediate position between the two forms· the fact implies, however, a possibility of dimorphism   Diagram fig 14 and fig. 15 represent a structure
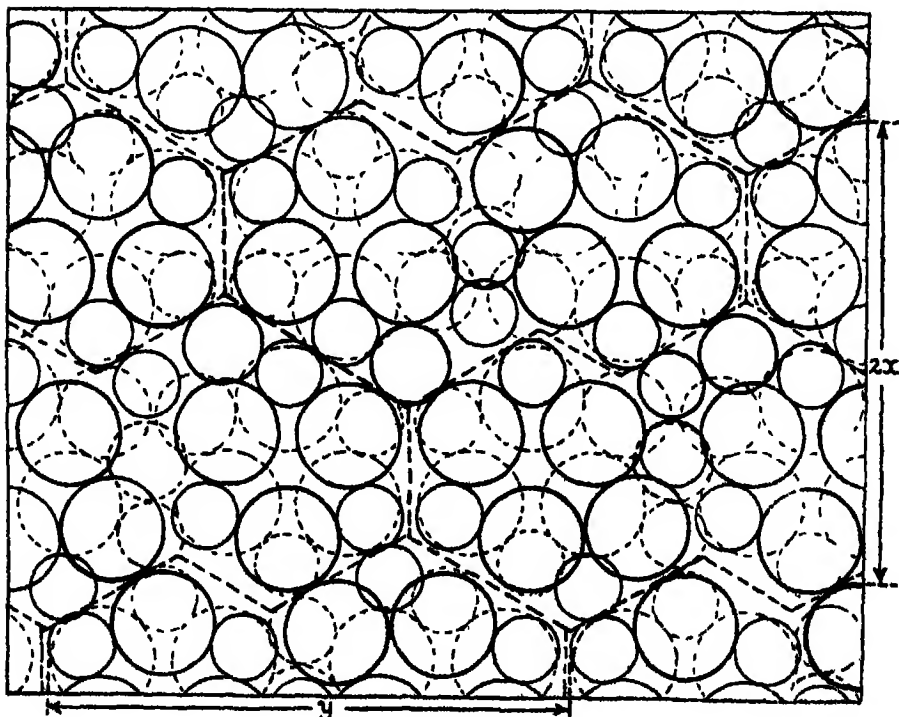
Fig 14.

formed by the displacement of the hydrogen atom in the ortho-position to the nitrogen atom situated between the two benzene units in the molecule,
a more closely packed structure is obtained when the methyl group takes up this position than when it occupies the other ortho-position   The diagram indicates the manner in which such molecular units of benzenesulphonorthotoluidide can be packed together in a plane layer.   As in the case of benzenesulphanilide, successive layers probably consist of enantiomorphous units.   If the third layer consist of units of the same kind as the

Fig 15

first rotated through an angle of 180° about an axis parallel to the direction of y, the fourth layer being similarly related to the second, a structure is obtained having three axes of symmetry at right angles but no planes of symmetry   This structure may correspond to orthorhombic benzenesulphonorthotoluidide.

Benzenesulphonorthotoluidide crystallises in the orthorhombic system, $a . b   c = 0\,7780   1   0\,5910$ Taking $3a$ and $4c/3$, the valency volume being 74, the equivalence parameters become $x   y   z = 3\,427   7\,999   2\,700$ If we suppose the vertical dimension in the diagram to be 2 700, those of x and y are found to be 3 44 7 96   These agree quite satisfactorily with the observed values and we seem therefore to have arrived at a satisfactory solution of the structure of the orthotoluidide   The 2 5 chlorobromo-benzenesulphonorthotoluidide described in Part II of these Studies appears to have a similar structure, its equivalence parameters being

$$3\,3368   8\,1238   2\,7917 ,   \beta = 102°\, 5'.$$

It can be seen that the effect of introducing the methyl group into the structure of benzenesulphanilide in the ortho-position is to lengthen both x and y parameters to about an equal extent.

Benzenesulphometatoluidide.—The diagram fig 16 illustrates the manner in which molecules of benzenesulphometatoluidide can be packed together. The same procedure having been adopted in deriving this structure from that of the sulphanilide as in the case of the orthotoluidide, no further explanation is necessary.   It may be remarked, however, that the methyl group of each molecule is found to intrude considerably into the domain of the neighbouring molecule; the four valencies of each methyl carbon atom in the assemblage are distributed approximately tetrahedrally.
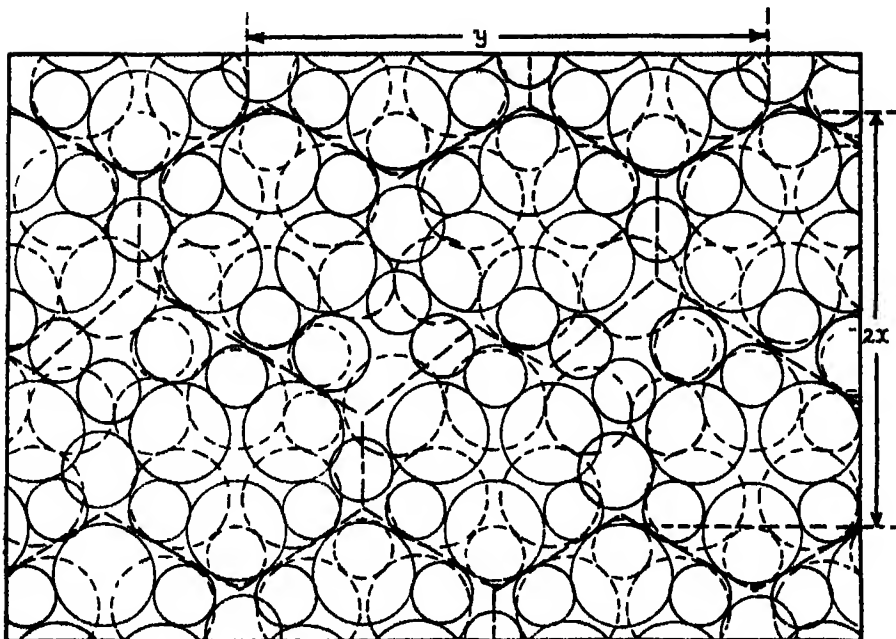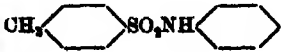
Fig 16
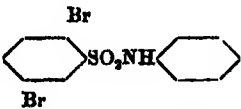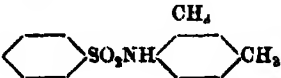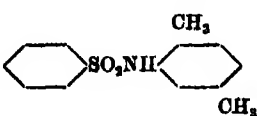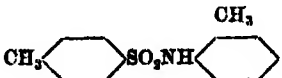
2 5 Chlorobromobenzenesulphometatoluidide crystallises in the monosymmetric system, a b c = 0·7576 1 1 1546 , β = 100° 37'   The equivalence parameters, taking $4a$, are x $y \cdot z$ = 3 2114 8 4287 2 7815   The dimensions of the diagram, as drawn from the model, are x y z = 3 25 8 18 2·78. The correspondence between the two sets of dimensions is very close and becomes even closer if allowance be made for the interaxial angle β, as 8 4287 sin β = 8·285.   Comparing these dimensions with those of the sulphanilide, it is obvious that the result of displacing the hydrogen atom in the meta-position by methyl is to increase y considerably and x but very slightly

A consideration of fig. 13 shows that the displacement of either the meta- or para-hydrogen atom in the aniline radicle by methyl would produce almost identical changes in the dimensions of the structure, namely a considerable elongation of y and very little change in x It has not, therefore, been deemed necessary to draw a diagram representing the structure of benzenesulpho-paratoluidide, it is sufficient to show that the equivalence parameters of such compounds as we have examined bear out our statement.   The following examples illustrate this point :—

	x	y	z	β
⬡SO₂NH⬡CH₃	3 3240	8 2028	2 7293	96° 3′
CH₃⬡SO₂NH⬡	3 2660	8 4145	2 7277	99 11

It can be seen that it makes little difference to the structure whether the methyl group be attached to the one or to the other phenyl group
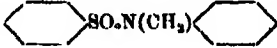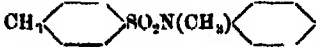
It may be anticipated that the effects upon the structure of benzene-sulphanilide of methyl groups in various positions will be cumulative when two or more groups are introduced together. For instance, if methyl groups be introduced into both ortho- and meta- or ortho- and para-positions, an elongation of both x and y parameters is to be expected. The following examples demonstrate this —

	x	y	z	β
Br⬡Br SO₂NH⬡	3 234	7 631	2 781	97° 50′
⬡(CH₄)SO₂NH⬡CH₃	3 6802	8 0318	2 7293	97 25
⬡(CH₃)SO₂NH⬡(CH₃)	3 3485	8 8622	2 7555	101 56
CH₃⬡(CH₃)SO₂NH⬡	3 4406	8 4733	2 7440	90 0

Unfortunately tolueneparasulphoparatoluidide crystallises in the anorthic system and consequently its axial directions cannot be determined but we should expect to find in this case a considerable extension in the direction of y and practically none in that of x

The displacement of the imino-hydrogen atom in benzenesulphanilide by the methyl group should produce an increase in the direction of x, the further introduction of a methyl group in the para-position should leave x

unchanged and increase the parameter y This is exactly what happens, as the following figures show —

	r	y	z	β
$\langle\!\!\langle \rangle\!\!\rangle SO_2N(CH_3)\langle\!\!\langle \rangle\!\!\rangle$	3 5888	7 5134	2 7890	100° 15'
$CH_3\langle\!\!\langle \rangle\!\!\rangle SO_2N(CH_3)\langle\!\!\langle \rangle\!\!\rangle$	3 5237	8 0074	2 8392	87 6

The results arrived at in this section are summarised in Table III   It may be noticed that in all cases the z value approximates very nearly to that of benzene

The y values vary from 7 513 to 8·86 , they are therefore 0 553–1 90 in excess of twice the y value of benzene, $3·480 \times 2 = 6 960$ When the changes in composition are considered with reference to Diagram 13 (benzenesulphanilide) and the manner in which the substitution is effected in various regions of the molecule of benzenesulphanilide is taken into account, it is obvious that the increase in the value of the y axis is of the character to be expected throughout the series

As is indicated by the same diagram, the change to be expected in the x parameter is relatively small in most cases, actually the values deduced (3 2114–3·680) are but slightly in excess of the x value of benzene, 3 101

Disulphanilides.—Benzenemetadisulphanilide has a crystal structure apparently very similar to that of benzenesulphanilide.   The accompanying diagram, fig. 17, shows the probable configuration of a unit of this substance.
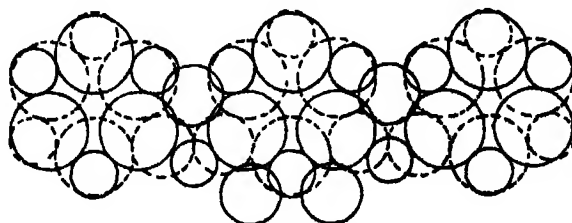
|FIG 17

The y dimension of a structure built up of such units should have a value about 3/2 times that of benzenesulphanilide   The actual equivalence parameters of the meta-compound deduced are x $y . z = 3·239 \cdot 13 035 : 2·515$, the low value thus found of z is noteworthy and in a measure unsatisfactory.

The structure of benzeneparadisulphanilide is apparently very similar to

that of the metadisulphanilide ; a comparison of the equivalence parameters of the two compounds in Table III shows them to be almost identical. A ready explanation of this observation is immediately forthcoming, for if the unit of the meta-compound of fig 17 be compared with the unit of the para-compound of fig 18, it can be seen that the configuration of the unit is
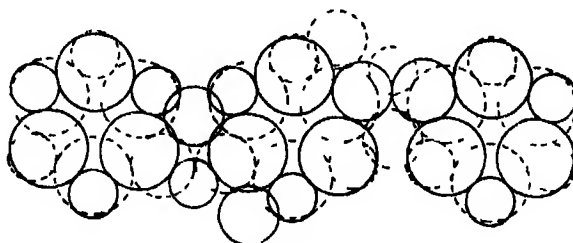
Fig 18

practically the same whether the three benzene units are linked through meta- or para-positions

The Structure of Acetanilide and allied Compounds

The cases previously considered have been either simple substitution derivatives or compounds such as benzenesulphanilide containing two benzene nuclei, more or less modified by substitution in the present section, the effect of introducing acid radicles of paraffinoid type into aniline and its derivatives will be considered

Models of the unit of acetanilide of appropriate size may readily be packed together but it will be noticed that the margins of the units in the region occupied by the acid radicle interpenetrate to an extent not noticeable in previous cases The form and dimensions of a plane layer of the assemblage are shown in fig 19.

The axial ratios of acetanilide are—a b c = 2·0670 1 0 8488, the symmetry being orthorhombic. taking $2a/3$, the equivalence parameters are —x . y z = 4 6862 : 3·4007 2 8865.

The diagram is drawn accurately to these figures Attention may be called to the fact that, as was to be expected, the y and z values are those of benzene, the x axis alone being elongated and to a considerable extent.

The axial ratios and equivalence parameters of a considerable number of compounds of the series are given in the following table. The figures indicate—(1) that the hexagonal marshalling of benzene units is retained in the structures, z being slightly above the benzene value 2 780 , (2) the value of y is scarcely affected by the introduction of alkylic radicles into the amino-group, (3) the introduction of alkylic groups increases only the

L 2
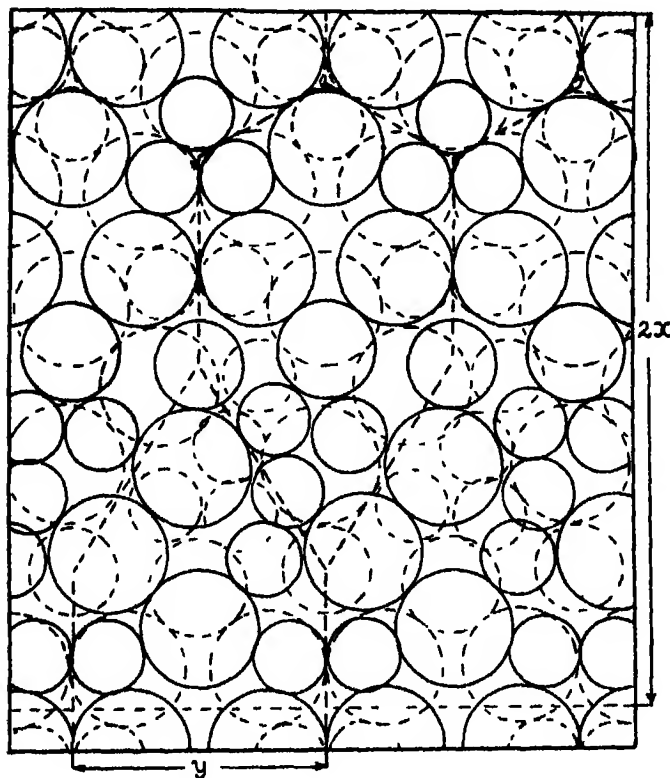
Fig 19

x parameter. It is clear when the model structure of acetanilide is examined, that alkylic groups can be introduced without disturbing the dimensions of the translations y or z It will be observed also that the structure of parabromoformanilide is very similar to that of formanilide.

	a	b	c	β		W	Fractions used	x	y	z
Formanilide	2 188	1	2 403	94°	54′	40	$2a/3, c/2$	4 1426	3 ·4123	2 8400
Parabromoformanilide	1 1028	1	1 4100	90	0	40	$3b/2$	3 8682	3 ·6362	2 8440
Acetanilide	2 0670	1	0 8488	90	0	46	$2a/3$	4 6862	3 ·4007	2 ·8865
Methylacetanilide	0 3953	1	0 8494	90	0	52	$4a$	5 3491	3 3880	2 ·8734
Ethylacetanilide	1 0064	1	0 8401	90	0	58	$5a/3$	5 7913	3 4527	2 9006
Propylacetanilide	1 3204	1	0 8410	90	0	64	$3a/2$	6 ·7038	3 3693	2 ·8835

It is noteworthy that in the case of the monosubstituted compounds the z value is very low, even lower than is observed in the case of sulphonates , the y value, on the other hand, is unusually high

Parachloracetanilide	1 8263	1	0 6804	90° 0'	46	—	4 9177 : 3 7076 : 2 5227
Parabromacetanilide	1 3904	1	0 7159	90 0	46	—	4 9696 3 5857 2 5691
Pariodacetanilide	1 4185	1	0 7415	90 29	46		4 9978 3 5233 : 2 6124
Parabromethylacetanilide	1 4063	1	1 5686	95 35	58	$a/2$	5 8863 3 7525 2 6884
Parabromopropionanilide	0 4466	1	0 8948	90 0	52	$2c/3$	5 8013 3 4604 2 5902
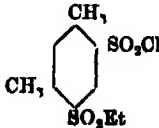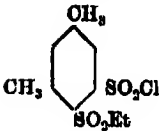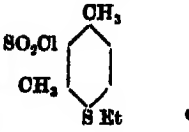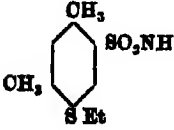
In the di-substituted acetanilides, however, there is a return to the larger value of z and the lower value of y

2 4 Dichloracetanilide	0 8263	1	0 6827	77° 33'	46	$2c$	4 7006 3 4428 2 8448
2 4 Bromochloracetanilide	0 8214	1	0 7074	77 46	46	$2c$	4 8588 3 4342 2 8206
2 4 Dibromacetanilide	0 8131	1	0 6895	78 24	46	$2c$	4 7884 3 4729 2 8240

Derivatives of Metaxylenothiol

The compounds to be referred to in this section were prepared and measured by Dr G Harker and will be described in a separate communication

In devising homogeneous closely packed assemblages of spheres to represent structures so complex as the substances under consideration, the difficulties encountered are very considerable The exact interpretation to be put upon the axial ratios is therefore somewhat uncertain and the equivalence parameters given in the following table are only put forward tentatively as those

	a	b	c	β	W	Fractions used	x	y	z
CH₃ / SO₂Cl / CH₃ / SO₂Et	1 0499	1	1 1806	90° 0'	66	$3c/2$	4 6038	5 0059	2 8268
CH₃ / SO₂Cl / CH₃ / SO₂Et	0 6856	1	0 7410	80 9	66	$2b/5$	4 7361	5 1189	2 7632
CH₃ / SO₂Cl / CH₃ / S Et	0 9942	1	0 6214	92 27	62	—	4 6205	4 6485	2 8885
CH₃ / SO₂NH₂ / CH₃ / S Et	0 7374	1	0 8882	75 28	66	$b/2$	4 3705	5 2641	2 9034

which appear to be rational, in order to show that the method is applicable in cases of this character

The dimensions of the eqivalence parameters agree, so far as we have been able to ascertain, with the dimensions of model structures constructed on the lines of those already described   It may be mentioned that several compounds allied to those considered by us were measured by Dr Harker which crystallised either in anorthic or pseudotetragonal forms
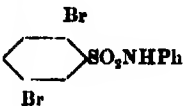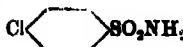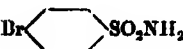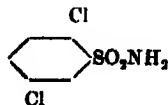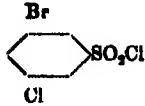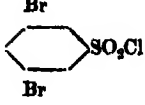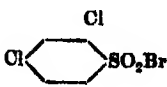
Anorthic, Pseudocubic and Pseudotetragonal Forms

Of the large number of benzenesulphochlorides containing halogens which have been examined, not a few crystallise in the anorthic system, this being the case particularly in the 1 3 4 and 1 3 5 series studied by Jee   As anorthic crystals possess no elements of symmetry, it is impossible to identify any principal directions in the crystal structure   no attempt can be made, therefore, at present, to interpret the structure of such crystals

Another class of crystals which cannot be dealt with includes all those of exceptionally high symmetry which approximate to cubic or to tetragonal symmetry   Such crystals are probably very closely related in structure to the cubic closely packed arrangement of equal spheres and in all probability, in such cases, the cubic or tetragonal space lattice contains several chemical units differing in their orientation   The identification of the translations in the crystal structure, in such cases again, is a matter of impossibility, at present

But the fact that such forms are met with frequently is of little effect on the argument, as it is possible to interpret the structure of substances closely allied to the forms which are anorthic, and in not a few cases, if not connected by transition forms with members of their series of determined structure, the anorthic forms may be caused to assume forms of determinable structure by crystallising them with substances with which they are isopolymorphous—a proof that they differ but slightly from the terms of recognised structure The argument is equally applicable to pseudocubic and pseudotetragonal forms

Table IV —Compounds which cannot at present be " Interpreted " Crystallographically

	a	b	c	β	W	Fractions used	x	y	z
				Pseudotetragonal					
(phenyl)SO₂NHPh	1	1	2 4324	90° 0′	68	—	7 3824	3 ·0350	3 ·0350
Br (phenyl)SO₂NHPh, Br	1 329	1	1 ·025	97 58	68	$2a$	7 793	2 932	3 005
Cl (phenyl)SO₂NH₂	0 ·620	1	0 603	97 48	40	—	4 739	2 ·981	2 858
Br (phenyl)SO₂NH₂	0 628	1	0 601	98 56	40	—	4 752	2 984	2 856
Cl (phenyl)SO₂NH₂ Cl	0 4233	1	0 4208	91 44	40	$2b/3$	4 6394	2 ·9455	2 ·9284
				Pseudocubic					
Br (phenyl)SO₂Cl Cl	1 3522	1	2 0367	89° 8½′	36	$3a/4, c/2$	3 3130	3 3675	3 2341
Br (phenyl)SO₂Cl Br	1 ·0696	1	0 4951	90 57	36	$2c$	3 4650	3 2395	3 2077
Cl (phenyl)SO₂Br	1 901	1	1 527	91 34	36	$a/2, 2c/3$	3 1746	3 3852	3 3963

Anorthic

	a	b	c	α	β	γ
Cl, Cl (phenyl)SO₂Br	0 ·58416	1	0 ·79742	85° 27′	89° 33′	54° 32′
CH₃ (phenyl)SO₂Cl	0 7669	1	1 ·1251	96 44	116 44	84 28
CH₃ (phenyl)SO₂NH(phenyl)CH₃	1 ·0525	1	0 ·9830	74 52	77 8	88 25

Summary

We venture to think that the evidence we are able to submit in this communication is conclusive proof of the validity of the postulates upon which Barlow and Pope have based their method of correlating crystalline form with internal molecular structure and of the general accuracy of their conclusions, at least in the case of benzene and its immediate derivatives.

It cannot be doubted that the establishment of a connexion between external and internal configuration is a step forward of immense consequence and that many problems hitherto beyond our reach may now be taken into consideration—especially the inquiry into the internal structure of the simpler compounds which have so long defied analysis   Hitherto crystallography has been little more than a descriptive science but it is to be expected that, in the near future, it will prove to be an all important and indispensable adjunct to chemical inquiry into both intramolecular and intermolecular structure

Meanwhile there are some considerations to which it is desirable to draw immediate attention

The Formula of Benzene and the Disposition of the Affinities of the Carbon Atom

Chemists are accustomed to represent benzene by a plane symbol and of late years it has been fairly generally admitted that the properties of the hydrocarbon are best expressed by the centric formula   In point of fact, this formula is practically the projection of the Barlow-Pope solid model representative of the interatomic structure and configuration of benzene arrived at by compressing the two layers into one plane, so as to exhibit the disposition of the carbon atoms in a " ring "

In passing from plane to solid formulæ, on the other hand, if we are logical, we must give to these latter as full a meaning as we have been accustomed to give to the plane formulæ   in other words, the solid units must be considered to be endowed with the properties which are regarded as characteristic of the elements they represent   It is generally recognised that the van't Hoff tetrahedral symbol of carbon is a symbol of extraordinary significance and there can be little doubt that it is truly representative of certain fundamental properties of the carbon atom, particularly of the disposition of the four affinities   more especially of the fact that these affinities operate within and without the atom in certain directions . those represented by lines drawn from the centre of mass of the regular tetrahedron to its four

apices · lines which meet, therefore, at an angle of 109° 28' and in the manner shown in fig 20.

As Barlow and Pope point out, when the carbon units are dissected out from their models, in the case of paraffinoid (open chain) derivatives, the directions in which affinity acts—those in which the various atoms are attached in the solid models—are those recognised by the van't Hoff hypothesis

It is owing to the fundamental property referred to that the carbon atoms in carbon compounds generally, not only in benzene, become arranged not in single layers in a plane but in zigzag fashion, in two superposed planes Thus, in the case of camphor, for example, the crystalline structure can be regarded as derived from an hexagonal closely packed assemblage of equal spheres arranged in two layers

If two layers be selected from an hexagonal assemblage of equal spheres, in the plane perpendicular to the hexagonal axis, and if from one of these layers alternate spheres be removed in two rows out of three, the remaining assemblage is immediately partitionable into units of 10 spheres so constituted as to simulate the arrangement of the carbon atoms in the camphor molecule but more opened out than in benzene. A structure thus derived would probably possess trigonal symmetry As a matter of fact, camphor is trigonal and several of the derivatives are pseudotrigonal

The dimension in the direction of the trigonal axis appears, from the model, to be close to the z value for benzene The parameters of camphor and several of its derivatives which we have been able to deduce are in accordance with this view —

	a	b	c	Fractions used	x	y	z
Camphor	0 860	1	1 6851	$c/8$	4 2625	4 ·9220 : 2 7647
aa Dichlorocamphor	1 4830	1	1 8365	·	4 ·1106	5 0904	2 7718
aa Dibromocamphor	1 5409	1	1 9043	—	4 1027	5 3096 : 2 ·6625
aa Bromochlorocamphor	1 5379 : 1	1 8355	—	4 2117	5 ·0373	2 7389
a Chlorocamphor	0 9707	1	1 2079	$2a/8$	4 2048	5 ·0789	2 7210
		$\beta = 93° 15'$					

As, therefore, it is to be expected that a dimension very near to the z dimension of benzene will be met with outside the benzene series, our demonstration that not only the z value of benzene but also the y value s characteristic of so a large a number of benzene derivatives is of special interest and value, as definite proof that the postulates on which the Barlow-Pope theory is based are sound the variations in dimension of the

x and y values which are the outcome of the various changes in composition to which we have referred are equally of value and interest in this connexion

But if the structure of benzene and benzenoid compounds be as suggested, the affinities of the carbon atoms cannot possibly meet at the natural angle (109° 28′)   It must, therefore, be supposed either that they do not act, within and from the atom, rigidly at a definite angle but are more or less deflected and strained · or that if they are so directed, interacting affinities do not overlap and neutralise each other but remain more or less unneutralised   The former view is practically that put forward by von Baeyer, the latter being that advocated by one of us.   The behaviour of benzenoid compounds is more in accordance with this latter point of view
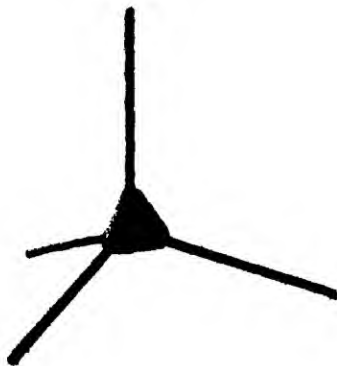
Fig. 20   Fig 21

In the case of benzene, the interacting affinities, including those by which the hydrogen atoms are held, must be so directed, in the case of each carbon atom, that three are projected into one and the same plane, the fourth affinity of each carbon atom will then be directed into an opposite plane   The result is that a bundle of three affinities—Faraday tubes or lines of force—emerges from each face of the benzene molecule, practically at right angles to the plane of the molecule, as shown in fig. 21   These are the "centric" affinities, it may be supposed   and it is their interaction apparently which gives benzene its special character.   Each affinity in the upper plane is balanced by a corresponding affinity in the lower plane but the two sets of affinities interpenetrate if projected upon a central plane.

The conclusion which we have been accustomed to draw, that the carbon atoms in benzene are united in a "ring" and nearly saturate one another is

thus seen to be incorrect the stability of the hydrocarbon cannot be due to the fact that the affinities meet at nearly the natural angle (109° 28') but is rather to be ascribed to the influence exercised by the "centric" affinities the unsaturated character of benzene is probably due to the unsatisfied affinities above referred to at the periphery of the molecule, which may be regarded as the active region.

If this view be applied in other cases important consequences follow Thus
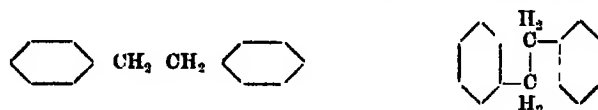
it is customary to represent the hydrocarbons dibenzyl, stilbene and tolane by symbols such as the first but the arrangement is more nearly that of the second given above in this latter figure, bearing in mind that in the case of each pair of carbon atoms in benzene the two atoms which are combined are in different planes, the two carbon atoms which unite the two benzene residues are shown in different planes Crystallographically the three compounds are very closely related – –

		a	b	c	β	W	Fractions used	x	y	z
Dibenzyl	$C_2H_4Ph_2$	1 8938	1	0 ·6261	81° 24'	70	$3b/4$	3 2265	8 1468	2 6935
Stilbene	$C_2H_2Ph_2$	1 9970	1	0 7026	84 38	68	$3b/4$	3 ·0141 : 8 0250	2 8236
Tolane	C_2Ph_2	2 ·0197	1	0 6800	82 45	66	$3b/4$	3 ·0091	8 1036	2 7285

Apparently the differences in the arrangement of the assemblage conditioned by the presence or absence of either two or four hydrogen atoms are but slight, the dimensions of the x and z parameters being very nearly those of benzene, the y parameter showing an increase such as is to be expected But taking into account the direction in which affinity acts in tolane from the benzene units towards the pair of carbon atoms at the junction, each of these latter must be supposed to have an affinity free, the which affinity is directed outwards · presumably these free affinities produce a disturbance in the fields normally existent at each surface of the two benzene residues If this be a correct conclusion, the central carbon atoms in tolane cannot be and are not combined in the manner commonly supposed by three affinities of each but at most by two, as in ethenoid compounds [*]

[*] It may be remembered that it has been contended by Julius Thomsen that the carbon atoms are less firmly held together in ethylene than in ethane and still less firmly in acetylene; *cf.* 'Phil Mag,' vol. 23, p. 73 (1887)

There are many directions in which it will be desirable to pursue the inquiry into the correlation of crystalline form with molecular structure and with physical and chemical properties it is already clear, that when the solid configuration of the molecules is taken into account, not a few of the problems which have occupied attention of late years will meet with a simpler solution than it has been possible to give to them hitherto The discussion of these matters and of the camphor and naphthalene derivatives, however, is reserved for a future communication

Experimental Material

1 4 **Series**, Nos 1–14 —The compounds numbered 1–14 in Table I, p 121, are all included in the same order in the table given on p. 1590 of the second of these Studies* but Nos 13 and 14 are Nos 14 and 15 in that table, as No 13, the compound SO_2Cl I $Cl = 1$ 2 5, the "inversion-form" of No 10, is omitted from the table now given Of the 15 sulphochlorides of the para-series previously considered, this is the only one for which we have not been able to deduce parameters in agreement with those given by other terms of the series we have again prepared and measured the substance without discovering any error in the previous measurements but in so doing we have noticed that this chloriodo-chloride is dimorphous, the second form, however, is labile and crystallises in the anorthic system It may be noted that the compound SO_2Cl Br I $= 1$ 2 5 (No 12) is also dimorphous but the stable second form of this substance has not been obtained from solution, the change taking place after removal from the liquid The two compounds referred to are the only instances of dimorphism yet observed in the 1 4 series.

14 *Diiodobenzenesulphochloride* (SO_2Cl 1 I $- 1$ 2 5)

System Monosymmetric
Axial ratios a b $c = 0.851$ 1 0.673 $\beta = 95° 46'$
Forms present $a\{100\}$, $b\{010\}$, $n\{120\}$, $p\{012\}$

Angle	No of observations	Limits	Mean
010 : 120	24	30° 15'—30° 45'	30° 34'
012 010	22	74 0 —75 9	74 33
012 120	18	59 16 —60 6	59 25

1 3 **Series**, Nos 15-19 —With the exception of No 19, these were all prepared and measured by E O Jee, D Sc. Of the eight compounds of the 1 3 4 series obtained by Dr Jee, three crystallise in the anorthic system and cannot therefore be included in the present discussion, the eight form an isotrimorphous series, as shown in the table on p 149

* 'Chem Soc Trans,' 1910

	Orientation			Crystallographic systems		
	1	3	4	Anorthic	Orthorhombic	Monosymmetric
I	Cl	Cl	SO₂Br	Stable	—	—
II	Cl	Br	SO₂Br	Stable	—	—
III	Br	Cl	SO₂Br	Stable	—	—
IV	Br	Br	SO₂Br	Labile →	Stable	—
V	Br	Br	SO₂Cl	(Labile) →	Stable	Labile
VI	Br	Cl	SO₂Cl	—	Stable	Labile
VII	Cl	Br	SO₂Cl	—	Labile →	Stable
VIII	Cl	Cl	SO₂Cl	—	Labile →	Stable

In the case of No V, the existence, in addition to the labile monosymmetric form which has been isolated and measured, of a labile anorthic form is inferred from the change observed under the polarising microscope as the substance cools from the melting point to the atmospheric temperature, as well as from the position the compound occupies in the series, coming, as it does, immediately below the dibromo-sulpho-bromide of which an anorthic form was isolated In all other cases, two forms were actually isolated

15 *Dichlorobenzenesulphochloride* (SO₂Cl Cl Cl = 1 2 4)

This separates from solution in a mixture of benzene and petroleum spirit (B P above 100° C) in massive monosymmetric tablets (fig 22) well suited for measurement The quality of the images obtained from the various forms was generally good
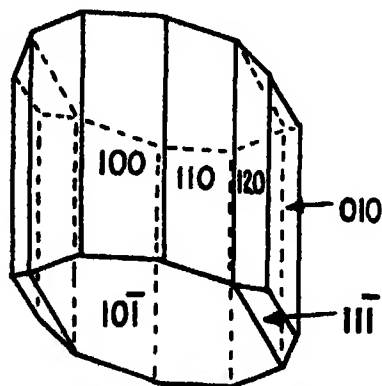
FIG 22 —15 Dichlorobenzene-sulphochloride
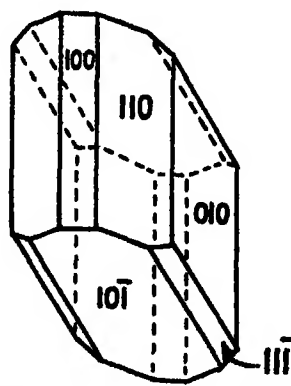
FIG 23 —16 Chlorobromobenzene-sulphochloride.

Found Cl 43 23 per cent , theoretical 43 3 per cent.
Forms present a{100}, b{010}, r{$\bar{1}$01}, o{$\bar{1}$11}, m{110}, n{120}
System . Monosymmetric.
Axial ratios a b c = 0 8342 1 0 5700   β = 97° 14½′

The optic axial plane is the plane of symmetry, optic axes emerging nearly normally from the faces a{100} and r{$\bar{1}$01} The optic axial angle is large and the double refraction strong

There is a good cleavage parallel to r{$\bar{1}$01}.

Evidence of the dimorphous character of the substance was obtained by crystallising it in a thin film on a microscope slide and observing under the microscope the gradual change of the labile form, in which the substance first crystallises, into the stable form

The following measurements were made —

Angle	No of observations	Limits	Mean	Calculated
ī01 ī11	64	26° 5'— 26° 56'	26° 25½'	—
ī00 ī01	33	60 20 — 60 54	60 40½	—
100 110	38	39 10 — 39 53	39 36½	—
ī01 110	24	67 40 — 68 12	67 53½	67° 50'
010 ī11	20	63 26 — 63 52	63 33½	63 34½
110 ī20	26	18 40 — 19 40	19 12	19 15½
010 : ī20	16	30 40 — 31 40	31 22	31 8
ī11 110	10	51 14 — 51 48	51 34	51 34
100 ī11	10	63 45 — 64 0	63 54	63 59
ī01 ī20	6	75 21 — 75 27	75 23½	75 19½
1ī0 110	6	79 8 — 79 40	79 16	79 13
010 : 110	12	50 13 — 50 44	50 26	50 23½
ī20 120	10	62 6 — 62 21	62 12	62 16
100 010	8	89 47 — 90 12	89 58	90 0
ī11 ī20	3	127 19 —127 30	127 22	127 35
100 120	4	58 50 — 59 5	58 56	58 52
ī11 1ī1	6	52 47 — 52 53	52 50	52 51

16 *Chlorobromobenzenesulphochloride* (SO₂Cl Br Cl = 1 2 4).

This is somewhat difficult to obtain in well defined crystals, it separates from a mixture of benzene and petroleum or of ether and ethylic acetate in monosymmetric tablets resembling the isomorphous dichlorobenzenesulphonic chloride but differing somewhat from the latter in habit (*cf* figs 22 and 23)

System   Monosymmetric
Axial ratios   *a* *b* *c* = 0 8352 1 0 5630   β = 97° 27
Forms present   *a*{100}, *b*{010}, *r*{ī01}, *m*{110}, *o*{ī11}

The optic axial plane is the plane of symmetry, an optic axis emerging normally to *r*{ī01} and another nearly normally to *a*{100}   Conclusive evidence of dimorphism was obtained, as in the case of the dichloro-compound, by microscopic observations

The following measurements were made —

Angle	No of observations	Limits	Mean	Calculated
ī00 ī01	26	61° 4'—61° 43'	61° 14'	—
100 110	19	39 19 —40 0	39 40	—
ī11 110	10	51 43 —52 24	52 4	—
ī01 110	27	68 0 —68 35	68 17	68° 15½'
010 110	15	49 51 —50 50	50 20	50 20
ī01 ī11	10	25 53 —26 46	26 14½	26 16
100 ī11	6	64 13 —64 38	64 25	64 26
010 ī11	4	63 22 —64 14	63 44	63 44

17 *Bromochlorobenzenesulphochloride* (SO_2Cl Cl Br = 1 2 4).

This was obtained in measureable form from benzene The habit of the crystals can be seen from fig 24

System Orthorhombic
Axial ratios *a b c* = 0 8182 1 0 5750
Forms present *c*{001}, *m*{110}, *r*{101}, *o*{111}

The crystals show a good cleavage parallel to *c*{001} Evidence of dimorphism was obtained by the formation of both orthorhombic and monosymmetric forms on crystallising it in admixture with the isomeric chlorobromobenzenesulphonic chloride

Angle	No of observations	Limits	Mean	Calculated
110 1Ī0	33	78° 20′—78° 53′	78° 35′	—
110 101	22	63 28 —63 45	63 35	—
101 111	8	24 54 —26 5	25 11½	25° 12½′
001 111	4	42 9 —42 22	42 15	42 14½
101 001	11	34 52 —35 30	35 5	35 5½
111 110	3	47 30 —47 58	47 43	47 45½
101 Ī11	1	72° 14′	72 14	72 8
101 Ī01	3	70° 3′—70° 11′	70 6	70 11
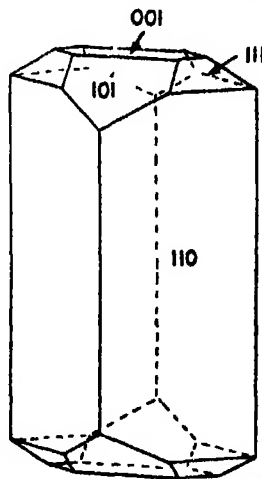
Fig 24 —17 Bromochlorobenzenesulphochloride

18. *Dibromobenzenesulphochloride* (SO_2Cl Br Br = 1 2 4).

This is obtained in crystals suitable for measurement from benzene mixed with a small quantity of high-boiling petroleum. In habit the crystals are similar to those of the isomorphous orthorhombic bromochlorobenzenesulphonic chloride but the elongation in the direction of the *c* axis is not so marked.

System Orthorhombic
Axial ratios *a b c* = 0 8134 . 1 0 5685
Found Br+Cl 58·36 per cent. ; theoretical 58·44 per cent.
Forms present *c*{001}, *m*{110}, *r*{101}, *o*{111}

There is a good cleavage parallel to $c\{001\}$ Conclusive evidence of dimorphism was obtained by the microscopic method

Angle	No of observations	Limits		Mean		Calculated	
110 1̄10	74	78° 0'—78° 35'		78° 15'		—	
101 110	88	63 15 —63 59		63 37		—	
101 111	25	24 49 —25 11		24 59		24° 59'	
001 111	11	41 32 —42 44		42 0		42 1	
001 101	10	34 45 —35 20		34 57		34 57	
111 110	18	47 50 —48 26		47 58		47 59	
101 1̄11	13	71 44 —71 59		71 52		71 51	
111 1̄10	11	97 44 —98 22		97 56		97 50	
101 1̄01	8	68 53 —70 37		69 51		69 54	
111 1̄11	4	62 26 —62 49		62 36		62 34	
111 11̄1	1	49° 56'		40 56		49 58	
111 1̄1̄1	1	84 6		84 6		84 2	

19 *Dibromobenzenesulphobromide* (SO_2Br Br Br $= 1$ 2 4)

This was obtained in two modifications, one orthorhombic and the other anorthic , only the former was measured completely   The orthorhombic crystals are indistinguishable from those of orthorhombic bromochlorobenzenesulphochloride (SO_4Cl Cl Br $= 1$ 2 4)   The anorthic form is the labile form at ordinary temperatures

System   Orthorhombic
Axial ratios a b $c = 0.7997$ 1 0.5627
Forms present $c\{001\}$, $m\{110\}$, $r\{101\}$, $o\{111\}$
There is a good cleavage parallel to $c\{001\}$

Angle	No of observations	Limits		Mean		Calculated	
110 1̄10	26	77° 12'—77° 29'		77° 18'		77° 18'	
110 101	67	62 59 —63 34		63 17½		—	
001 101	78	34 42 —35 44		35 8		—	
101 1̄01	22	70 7 —70 32		70 17		70 16	
101 111	24	24 27 —24 57		24 42		24 43	
110 111	8	47 51 —48 5		48 0		47 59	
010 001	2	89 53 —90 4		89 58		90 0	
001 111	4	41 51 —42 14		42 1		42 1	

1 2 Series, Nos. 20–27 —Five compounds of this series containing either chlorine or bromine or both were prepared and measured by H. Harding, B Sc   The dichloro- and chlorobromo-chlorides are alike in form , the dibromochloride has a distinct form but, as in the case of the 1 3 series, the chlorobromosulphobromide occurs in two modifications identical respectively with those of the chlorides referred to   In this series, much difficulty was experienced in effecting the measurements owing to the low melting points of the compounds.

The iodo-derivatives (Nos 25–27) were measured by A. R. Runeckles, B Sc

20 *Dichlorobenzenesulphochloride* (SO_2Cl Cl Cl $= 1$ 3 . 4).

This chloride crystallises from light petroleum in large flat plates elongated in a direction perpendicular to the zone [1̄01 1̄11] , crystals suitable for crystallographic

measurement are obtained only with great difficulty, usually the faces are rounded and do not give good reflections

System   Monosymmetric.

Axial ratios a $b . c = 1.6330$ 1   1 1540 $\beta = 105°\ 1'$

Forms present $a\{100\}$, $r\{10\bar{1}\}$, $n\{210\}$, $o\{111\}$, $w\{11\bar{1}\}$.

Angle	No of observations	Mean	Calculated
111 1$\bar{1}$1	24	92° 40'	—
111 $\bar{1}$11	20	50 7	—
$\bar{1}$01 $\bar{1}$11	29	39 13	—
$\bar{1}$01 111	8	76 15	76° 17'
111 11$\bar{1}$	21	74 6	74 7
100 11$\bar{1}$	9	56 44	56 47
100 111	8	73 8	73 8
100 : 10$\bar{1}$	1	45 2	44 57
$\bar{1}$11 · 11$\bar{1}$	4	101 35	101 34
10$\bar{1}$ 210	1	56 22	56 14
100 210	1	38 12	38 14

21   *Bromochlorobenzenesulphochloride* (SO$_2$Cl   Br   Cl = 1   3   4)

This compound crystallises in forms similar to those of the corresponding dichlorobenzenesulphochloride but is much more readily obtained in good measureable crystals , the two compounds are closely isomorphous.

System   Monosymmetric

Axial ratios a b $c = 1.6000$ 1   1.1390 $\beta = 106°\ 9'$

Angle	No of observations	Mean	Calculated
111 1$\bar{1}$1	16	92° 8'	—
111 $\bar{1}$11	26	50 48	—
$\bar{1}$01 $\bar{1}$11	22	38 25	—
$\bar{1}$01 : 111	17	76 22	76° 23'
111 11$\bar{1}$	17	74 43	74 45
100 11$\bar{1}$	15	55 50	55 48
100 111	19	73 26	73 24
100 10$\bar{1}$	4	44 7	44 10
$\bar{1}$11 11$\bar{1}$	9	103 8	103 10
10$\bar{1}$ 210	1	55 21	55 21
100 210	1	37 37	37 33

22.   *Bromochlorobenzenesulphobromide* (SO$_2$Br . Br . Cl = 1   3   4).

This compound is isomorphous with the two sulphochlorides previously described crystallising from a mixture of benzene and petroleum (B P 100° C) in forms similar in habit to those of the chlorides, though the form {210} was not observed.

System · Monosymmetric.

Axial ratios : $a . b . c = 1.6012$ 1   1 1410 $\beta = 105°\ 29'$.

Angle	No of observations	Mean	Calculated
111 1$\bar{1}$1	24	92° 4'	—
11] $\bar{1}$11	11	50 46	—
101 $\bar{1}$11	15	38 40	—
111 $\bar{1}$01	2	76 30	76° 28'
111 : 11$\bar{1}$	10	74 27	74 31
100 10$\bar{1}$	6	56 10	56 9
100 111	8	73 3	73 5
100 10$\bar{1}$	1	44 32	44 29

23 Bromochlorobenzenesulphobromide (SO_2 Br Cl = 1 3 4, second form)

This was obtained from a mixture of benzene and petroleum (B P 100° C) in very badly developed thin plates similar in habit and appearance to 3 · 4 dibromobenzene-sulphochloride

System   Monosymmetric
Axial ratios $a \cdot b$ $c = 1$ 2931 1 0 5855 $\beta = 77$ 30'
Forms present $a\{100\}$, $b\{010\}$, $m\{110\}$, $q\{011\}$

Angle	No of observations	Mean	Calculated
010 110	21	38° 23'	—
010 011	14	60 15	—
110 : 01$\bar{1}$	2	59 38	—
110 011	3	73 57	74° 12'
$\bar{1}$00 011	5	79 0	79 10

24 Dibromobenzenesulphochloride (SO_2Cl Br Br = 1 3 4)

This compound does not crystallise in the same isomorphous series as the three substances described previously, Nos 20–22   Good crystals were obtained, though with great difficulty, from a mixture of benzene and petroleum in the form of small flat mono-symmetric plates in which the form $b\{010\}$ predominates , very large micaceous plates were obtained from light petroleum   The crystals were dull and gave untrustworthy readings

System   Monosymmetric
Axial ratios a b $c = 1$ 2823 1 0 5762 $\beta = 76°$ 0'
Forms present , $a\{100\}$, $b\{010\}$, $m\{110\}$, $q\{011\}$, $r\{101\}$

Angle	No of observations	Mean	Calculated
010 110	63	38° 47'	—
010 011	32	60 48	—
110 011	10	75 38	—
110 01$\bar{1}$	8	59 12	59° 10'
110 101	4	82 27	82 29
011 101	4	38 0	38 21
100 110	37	51 12	51 13
011 01$\bar{1}$	15	58 8	58 24
100 010	6	89 59	90 0
010 101	2	89 44	90 0

25. *Iodochlorobenzenesulphochloride* (SO$_2$Cl I Cl = 1 3 4)

This compound appears to be dimorphous The usual form, which is not isomorphous with the corresponding diiodo-compound, has a flat tabular habit, the form c{001} being most prominent It crystallises from a mixture of benzene and light petroleum

System Monosymmetric
Axial ratios *a* *b* *c* = 1 1764 1 1·0294 β = 85° 29'
Forms observed c{001}, m{110}, n{210}, o{111}

Angle	No of observations	Limits	Mean	Calculated
110 1̄10	18	98° 35'—99° 37'	99° 3'	99° 6'
1̄10 110	22	80 13 —81 47	80 54	—
001 110	20	86 14 —87 38	87 4	—
110 001̄	22	92 21 —93 28	92 56	92 56
111 110	6	37 3 —38 7	37 35	—
111 001	5	55 5 —55 29	55 17	55 21
110 210	10	18 51 —19 31	19 1	19 9
210 2̄10	6	60 51 —60 57	60 52	60 48
111 210	2	42 47 —42 51	42 49	42 34
001 210	4	93 33 93 57	93 46	93 54
210 001̄	2	86 3 —86 6	86 5	86 6
111 1̄11	1	——	77 44	77 38

26 The second form of this substance was only observed upon one occasion, when a few needle-shaped crystals were obtained, the angular measurements proved these to be closely isomorphous with the crystals of the diiodo compound of the same series The prismatic needles were elongated in the direction of the *a* axis

System Monosymmetric
Axial ratios *a* *b* *c* = 0 5964 1 0 5823 β = 85° 21'
Forms observed b{010}, m{110}, o{111}

Angle	No of observations	Limits	Mean	Calculated
111 1̄11	5	46° 36'— 46° 57'	46° 48'	—
111 010	14	66 6 — 67 19	66 24	66° 36'
110 1̄10	3	61 20 — 61 35	61 29	—
010 110	4	58 31 — 60 3	59 16	59 15½
1̄10 111	2	70 45 — 72 14	71 34	71 2
1̄10 111	3	108 32 —108 50	108 39	108 58
111 1̄10	3	136 35 —137 8	136 53	136 57
110 111	2	42 52 — 43 14	43 3	—

27 *Diiodobenzenesulphochloride* (SO$_2$Cl I I = 1 3 4).

This compound crystallises from benzene in thin diamond-shaped plates, {010} being the dominant form

System Monosymmetric
Axial ratios *a* *b* *c* = 0 5968 1 0 5832 β = 85° 42'
Forms observed b{010}, m{110}, r{1̄01}, o{111}

Angle	No of observations	Limits		Mean		Calculated	
111 1Ī1	13	46° 35'— 47° 2'		46° 48'		—	
111 010	17	65 59 — 67 10		66 33		66° 36'	
110 1Ī0	8	61 12 — 61 52		61 31		—	
110 : 010	5	58 50 — 59 37		59 10		59 14	
110 111	2	42 50 — 42 55		42 53		—	
111 ĪĪ0	2	137 1 --137 4		137 3		137 7	
Ī01 110	4	51 5 — 51 14		51 8		51 25	
Ī01 111	2	88 53 — 88 54		88 53½		88 49	
Ī10 111	4	108 37 —108 55		108 49		109 2	

Nos. 28–30 are separately described by Mr. Mummery in a communication to the Chemical Society

31 *Dibromobenzenesulphochloride* (SO₂Cl Br Br = 1 2 6)

This substance crystallises in rectangular plates or long prisms.

System   Monosymmetric
Axial ratios $a b . c = 2\,1688   1   1\,9006   \beta = 78° 19'$
Forms present $a\{100\}, c\{001\}, g\{011\}, r\{101\}, o\{111\}$

Angle	No of observations	Limits		Mean		Calculated	
001 011	43	61° 30'—61° 58'		61° 45'		—	
Ī00 011	18	84 17 —84 40		84 30		—	
001 101	5	45 48 —46 31		46 13		—	
100 101	5	55 3 —55 44		55 22		55° 28'	
011 Ī01	7	70 38 —71 0		70 50		70 53	
Ī00 001	11	78 0 —78 34		78 17		78 19	
100 1Ī1	2	53 29 —53 48		53 38		53 37	
011 111	1	——		41 56		41 53	
111 101	1	——		49 38		49 51	
111 01Ī	1	——		58 53		59 16	

32 *Dichlorobenzenesulphobromide* (SO₂Br Cl Cl = 1 2 4)

This separates from a mixture of benzene and petroleum in anorthic tablets, the most prominent form being the pinacoid $a\{100\}$

Found   Cl + Br 52·0 per cent. C₆H₃Cl₂SO₂Br requires 52 per cent.
        Sulphobromine, 27·85 per cent. C₆H₃Cl₂SO₂Br requires 27 58 per cent.
System   Anorthic
Axial ratios $a b c = 0\,58416   1   0·79742   a = 85° 27', \beta = 89° 33', \gamma = 54° 32'.$
Forms present $a\{100\}, b\{010\}, c\{001\}, m\{Ī10\}, o\{1Ī1\}, d\{102\}$

Angle	No of observations	Limits	Mean	Calculated
001 102	25	38° 12′—38° 58′	38° 34′	38° 86¼′
100 102	20	48 13—48 57	48 30¼	48 27
100 001	80	86 46—87 31	87 3¼	—
001 1Ī1	102	54 17—55 7	54 43	—
010 001	91	84 11—85 8	84 34	—
1Ī1 102	27	35 1—35 34	35 16	—
100 1Ī1	65	51 45—52 25	52 5¼	—
010 102	28	64 3—64 30	64 17	64 15
100 010	40	54 20—54 44	54 33½	54 35¼
010 · 1Ī1	85	93 41—94 32	94 1	94 6¼
010 Ī10	11	80 46—81 33	81 9	81 11
Ī00 Ī10	11	44 14—44 84	44 24¼	44 23¼
Ī10 Ī1Ī	2	36 16—36 17	36 16¼	36 28
001 Ī10	2	—	88 52	88 49

33 *Bromochlorobenzenesulphochloride* (SO$_2$Cl Br Cl = 1 3 5)

Measureable crystals are obtained from benzene with some difficulty in the form of monosymmetric tablets (*cf* fig 25)   The crystals are generally obtained in fragments on account of the tendency for several to grow together

System   Monosymmetric (Pseudocubic)

Axial ratios   *a* *b* *c* = 1 3522 1 2·0367   β = 89° 8½″

Forms observed   *c*{001}, *r*{101}, *o*{111}, *w*{Ī11}

Angle	No of observations	Limits	Mean	Calculated
101 : 11Ī	50	74° 38′—75° 40′	75° 9′	—
001 : Ī11	37	64 34—69 11	68 52	—
101 001	80	55 24—56 5	55 49½	—
101 : 111	20	47 33—48 36	48 18	48° 11¼′
Ī11 11Ī	9	82 26—82 58	82 41	82 45
001 111	9	67 34—68 8	67 58	67 59
111 Ī1Ī	9	83 5—84 38	83 32	83 37
111 : 11Ī	8	43 2—43 4	43 3	43 9
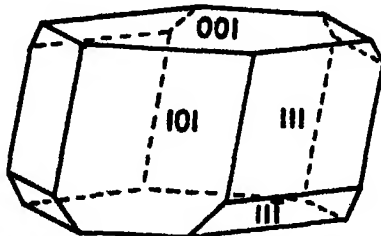
Fig. 25.—33 Bromochlorobenzenesulphochloride.

34. *Dibromobenzenesulphochloride* (SO$_2$Cl Br . Br = 1 3 5).

This compound crystallises from benzene or acetone in well formed octahedra. Crystals obtained from acetone or ether were sometimes found to be strongly pyroelectric but no hemimorphism could be detected in the crystals.

The habit of the crystals is variable (cf fig 26)　The usual combination is a{100}, n{210}, o{111}, b{010}, in addition w{Ī11} sometimes appears and suppresses a{100}, the form {Ī11} is always very poorly developed　No definite cleavage was detected

System　Monosymmetric (pseudocubic)

Axial ratios　a : b : c = 1 0696 : 1 : 0 4951　β = 90° 57'

Angle	No of observations	Limits				Mean		Calculated	
2Ī0 210	18	55	40'	56°	34'	56°	16'	—	
100 210	32	27	44	— 28	38	28	8½	28°	8
1Ī1 111	25	47	43	48	27	48	7	—	
111 Ī1Ī	28	131	28	132	20	131	53	131	53
111 010	11	65	39	— 66	15	65	57	65	56½
100 111	21	66	25	— — 67	8	66	45	—	
111 Ī11	6	44	24	- 45	2	44	44	45	4
Ī11 Ī00	2	68	25	68	44	68	34	68	11
210 111	15	57	7	— 57	46	57	22	57	18
111 2Ī0	14	122	13	—123	0	122	40	122	42
2Ī0 1Ī1	10	80	49	-- 81	25	81	0	81	2
1Ī1 2Ī0	10	98	34	— 99	28	98	56	98	58
Ī11 Ī1Ī	4	48	29	— 49	3	48	41	48	40
111 11Ī	4	67	30	- 68	16	67	50	68	15
010 Ī11	3	65	30	— 65	55	65	41	65	41
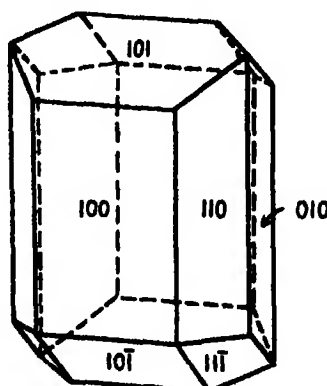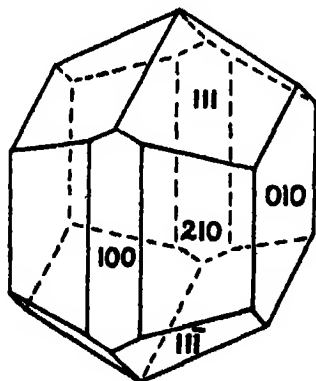
Fig 26 —34 Dibromobenzenesulphochloride　Fig 27 —36 Benzeneorthodisulphochloride.

35　*Tolueneparasulphochloride* (CH₃.C₆H₄ SO₂Cl)

Otto, who has already measured this compound,[*] gives no indication of the degree of accuracy of his measurements, the axial ratios he deduced are

$$a : b : c = 0 7682 : 1 : 1 1139$$
$$α = 97° 24', \quad β = 117° 6', \quad γ = 84° 28'$$

The crystals we have measured were deposited from benzene

System　Anorthic

Axial ratios　a : b : c = 0 7669 : 1 : 1·1251

$$α = 96° 44', \quad β = 116° 44', \quad γ = 84° 28'$$

Forms present　a{100}, b{010}, c{001}, m{110}, q{01Ī}, o{11Ī}.

There is a perfect cleavage parallel to b{010}.

* 'Ber,' vol 19, p. 1832.

Angle		No. of observations	Limits			Mean		Calculated	
010	110	11	57° 8'	- 57°	37'	57°	20'	—	
110	100	8	35 17	— 35	43	35	28	35°	28'
010	100	19	92 31	— 93	2	92	48	—	
100	0Ī0	18	87 0	-- 87	37	87	12	87	12
010 : 111		5	57 25	— 57	50	57	35	57	38
111	0Ī0	5	122 10	122	35	122	26	122	22
001	010	20	84 47	-- 85	31	85	14	—	
010	01Ī	8	46 52	47	14	47	1	47	5
01Ī	00Ī	7	47 37	— 47	57	47	44	47	41
010	00Ī	17	94 27	95	11	94	46	94	46
001	100	13	63 33	63	54	63	41	63	40
100	00Ī	14	116 7	116	30	116	20	—	
001	110	9	64 52	— 65	18	65	5	65	2
110	111	8	34 26	— 34	52	34	35	34	35
001	111	11	99 21	- 99	51	99	37	—	
111	00Ī	8	80 13	80	37	80	25	80	23

36 *Benzenorthodisulphochloride,* $C_6H_4(SO_2Cl)_2$

Good crystals were deposited from the solution in benzene   The habit is variable , sometimes the crystals are flat and tabular in form, growing on {010}   at others, long prisms elongated in the direction of the c axis (fig 27)

There is a good cleavage parallel to b{010}

System   Monosymmetric

Axial ratios a b $c = 1.5066$ 1 0.9061 $\beta = 90°$ 6'

Forms present a{100}, b{010}, m{110}, r{101}, p{Ī01}, o{111}

Angle		No. of observations	Limits			Mean		Calculated	
100	110	19	56° 21'	56°	32'	56°	26'	—	
110	010	19	33 25	— 33	39	33	34	33°	34'
100	010	18	89 56	— 90	5	90	0	90	0
Ī01	Ī11	18	37 41	– 38	7	37	51	37	51
Ī11	0Ī0	21	51 59	— 52	25	52	9	—	
Ī01	010	21	89 47	— 90	12	90	0	90	0
Ī00	Ī01	9	59 0	— 59	6	59	3	—	
Ī01	101	10	62 4	62	9	62	7	62	3
101 : 100		18	58 47	— 58	52	58	49	58	54
Ī00	Ī11	2	66° 0'			66	0	66	2
Ī11	100	2	114 0			114	0	113	58
101	Ī11	2	68° 11'	— 68°	21'	68	16	68	17
Ī11	10Ī	2	111 39	— 111	49	111	44	111	43

37. *Benzenemetadisulphochloride,* $C_6H_4(SO_2Cl)_2$ *

System .   Monosymmetric

Axial ratios a, b $c = 0.864$ 1 0.586 $\beta = 86°$ 5'

Forms observed a{100}, b{010}, m{110}, g{011}, o{111}, r{Ī01}

---

* R. C Gale, *cf* Otto, 'Ber.,' vol 19, p. 2424

Angle	No of observations	Limits.		Mean		Calculated	
010 011	25	48° 48'—	49° 55'	49°	20'	49°	14'
010 110	17	59 12 -	59 52	59	40	59	21
Ī00 011	15	86 37 —	87 22	86	57	86	56
011 : 01Ī	10	81 6 —	81 58	81	32		—
110 100	22	29 25 —	30 55	30	19		—
11Ī 100	11	40 30 —	40 55	40	42	40	43
01Ī 11Ī	10	45 37 —	46 35	46	7	46	13
100 011	14	92 48 -	93 20	93	4		-
100 10Ī	4	51 4 - .	51 22	51	11		
100 Ī01	5	128 42 –	129 11	128	55		-

38. *Metanitrobenzenesulphochloride,* $C_6H_4(NO_2)(SO_3Cl)$

This compound crystallises from a mixture of benzene and light petroleum in prisms with truncated ends (fig 28). The forms observed were *m*{110}, *q*{011}, *r*{101}, *p*{121} and *s*{Ī21}. There is an indifferent cleavage parallel to *r*{101}

System Monosymmetric

Axial ratios · *a b c* = 1 1989 1 0 4269 β = 89° 23'

Angle	No of observations	Limits		Mean		Calculated	
110 Ī10	15	79° 32'	79° 53'	79°	40'		--
Ī10 Ī10	15	100 9 —	100 29	100	20	100°	20'
110 101	18	77 45 —	78 7	77	56		—
101 0Ī1	5	29 48	30 12	29	57	30	0
0Ī1 Ī10	9	71 50 —	72 21	72	4		
110 121	3	49 57 —	50 4	50	0	49	50
121 : 011	3	22 51	23 5	22	57	23	0
110 011	6	72 41 —	73 4	72	49	72	50
011 Ī10	5	106 55 —107	9	107	3	107	10
011 0Ī1	1	——		45	58	46	14
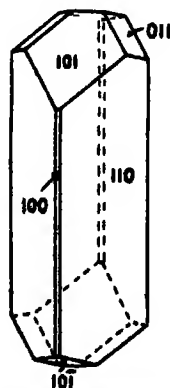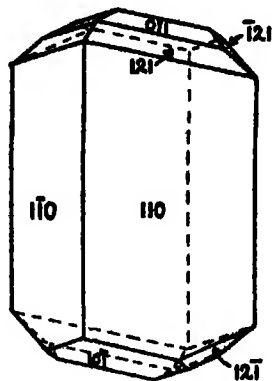
Fig. 28.—38. Metanitrobenzenesulphochloride   Fig 29 —40. Benzeneparadisulphochloride.

39. *Benzenemetadisulphonamide*, $C_6H_4(SO_2.NH_2)_2$.   (R. C Gale)

System · Orthorhombic.

Axial ratios a b $c = 2\,5086$ 1 0·9787

Forms observed $a\{100\}$, $c\{001\}$, $n\{120\}$, $o\{111\}$, $w\{121\}$

Angle	No of observations	Limits		Mean	Calculated
100 110	24	67° 39′	68° 53′	68° 18′	68° 16′
110 1̄10	18	43 4 — 43 54		43 28	—
100 001	18	89 34 90 36		89 58	90 0
100 111	41	73 41 - - 75 8		74 26	—
100 311	22	49 40 — 50 59		50 33	50 6
311 111	16	23 16 24 50		23 52	24 20
111 1̄11	16	32 18 30 21		30 59	31 8
311 1̄11	16	54 2 56 1		54 53	55 28

40 *Benzeneparadisulphochloride*, $C_6H_4(SO_2Cl)_2$.

This compound was prepared from potassium benzeneparadisulphonate by the action of a mixture of phosphorus tri- and pentachlorides.

After some trouble, good measurable crystals were obtained from benzene ; as a rule, the substance crystallises in four-sided prisms, terminated, at each end, by a single face Such crystals do not give sufficient data for the determination of the axial ratios, but other forms appear occasionally from which the necessary data may be derived (*cf* fig. 29).

The compound is described by Hollemann[*] as dimorphous, the transition point being 71 4° C   Conclusive proof of the dimorphism of the substance is obtained if a thin liquid film be allowed to cool slowly upon a microscope slide under a cover-slip   The film first crystallises in a transparent form, showing good colour effects when viewed under the polarising microscope ; in a few seconds, however, a change sweeps across it and it becomes opaque, the effect upon polarised light being then quite different Only one crystalline form has been isolated

System Monosymmetric.

Axial ratios a b $c = 1\cdot2261$ 1 0·6242. $\beta = 105°\,35'$

No cleavage could be detected.

Forms present $m\{110\}$, $r\{101\}$, more rarely $q\{011\}$, $s\{\bar{1}01\}$, $a\{100\}$

Angle	No of observations	Limits		Mean	Calculated
110 1̄10	14	80° 21′ 80° 39′		80° 31′	—
1̄10 1̄1̄0	12	99 18 — 99 42		99 29½	99° 29′
100 110	8	49 38 - 50 5		49 46	49 44½
101 011	8	38 0 — 38 15		38 6	—
011 : 1̄10	5	75 38 — 75 52		75 47	75 51
101 110	16	65 23 — 66 25		66 3	—
100 101	1	——		51 5	51 5
101 1̄01	1	——		52 0	52 56
1̄01 011	4	41 46 — 41 58		41 51	41 49½
011 110	3	57 11 — 57 16		57 14	57 10½
110 10̄1	4	80 47 — 81 10		80 57	81 0
011 0̄1̄1	2	62 1 - 62 3		62 2	62 2

* 'Versl Kon. Akad van Wetensch. Amsterdam,' 1906, p. 573.

41 *Benzeneparadisulphobromide,* $C_6H_4(SO_2Br)_2$.

At ordinary temperatures, this compound crystallises from benzene in a highly labile form but stable crystals are obtained if the solution be kept at 37° C

Analysis   Found 43 76 per cent bromine , theoretical 43 95 per cent
System   Orthorhombic
Axial ratios   *a*   *b*   *c* = 2 5084 1 1·0890
Forms present   *a*{100}, *r*{101}, *m*{110}, *n*{210}

Angle	No of observations	Limits		Mean	Calculated
100 101	21	66° 1′	66° 52′	66° 32′	46′ 56′
101 101	8	46 32	47 25	46 52	
100 101	15	113 13	-113 52	113 31	113 28
100 210	23	50 55	51 46	51 26	
100 110	15	67 51 — 68 27		68 14	68 16
101 210	6	75 28 — 75 48		75 40	75 37

42 *Benzenesulphanilide,* $C_6H_5 SO_2.NHC_6H_5$

This compound has been measured by L. Brugnatelli,[*] but as the data quoted by him were somewhat scanty, we have again examined the compound

System   Tetragonal
Axial ratios   *a*   *c* = 1 2 4324
Habit   Well formed octahedra from acetone or ethylic acetate, consisting of the form {112}, the form {001} appearing as a truncation   The form {111} was also observed Very massive crystals are frequently obtained (*cf* fig 30)

Brugnatelli could detect no cleavage but we find that the crystals cleave perfectly parallel to *c*{001}   A cleavage plate exhibits the figure characteristic of an uniaxial crystal

Angle	No of observations	Limits		Mean	Calculated
112 112	10	119° 21′	120° 11′	119° 42′	119° 38′
112 112	8	60 2 — 61 14		60 29	60 22
111 112	6	13 24	14 26	13 55	13 59
112 112	14	74 59	75 44	75 22	-
112 112	14	104 14 - 105 1		104 36	104 38

43 *Benzenesulphonorthotoluidide,* $C_6H_5 SO_2 NH.C_6H_4 CH_3$

In the endeavour to obtain measurable crystals many solvents were tried, including acetone, ethylic acetate, ether and chloroform ; the crystals had a great tendency to twin and the faces were generally striated   The best crystals were obtained from a mixture of acetone and ethylic acetate (fig 31)

System   Orthorhombic.
Axial ratios   *a*   *b*   *c* = 0 7780 1.0 5910
Habit : Flat plates are developed growing on {010}   Other forms present are {110}, {011}, and {210}   Faces very imperfect, especially {010}   Cleavage parallel to {010}

* 'Zeit. Kryst Min,' vol 30, p. 191

Angle	No of observations	Limits	Mean	Calculated
010 110	17	51° 39' 52° 46'	52° 7'	—
010 011	14	59 0 — 59 56	59 25	—
011 210	10	15 59 — 16 46	16 29	16° 38'
110 011	6	71 3 72 11	71 48	71 48
1̄10 011	6	107 35 — 108 48	108 8	108 12
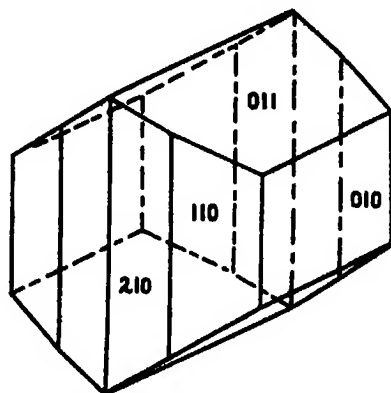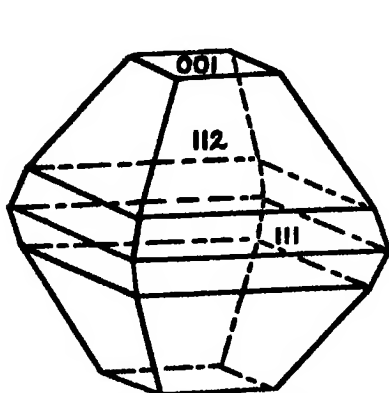
Fig 30 — 42 Benzenesulphanilide.　　Fig 31 — 43 Benzenesulphonorthotoluidide

44 *Benzenesulphopaiatoluidide*, C₆H₅ SO₂ NH C₆H₄ CH₃

System Monosymmetric

Axial ratios a b $c = 1\ 5028$ 1 1 8269　$\beta = 96°\ 3'$

Habit Crystallises from acetone in well-formed prisms (fig 32)

Forms present $c\{001\}, b\{010\}, r\{101\}, s\{\bar{1}01\}, n\{210\}, o\{111\}, x\{121\}, \gamma\{\bar{3}23\}$

Angle	No of observations	Limits	Mean	Calculated
1̄01 001	10	53° 44' — 54° 28'	54° 2'	54° 12'
001 101	12	46 41 — 47 27	47 2	46 59
101 10̄1	9	78 29 — 79 6	78 47	78 49
1̄01 3̄23	8	38 49 — 39 18	39 8	39 8
3̄23 1̄11	4	11 19 — 11 38	11 28	11 30
1̄11 · 1̄21	13	16 42 — 17 27	17 1	17 4
1̄21 · 010	10	21 53 — 22 30	22 17	22 18
1̄01 1̄11	22	50 12 — 50 59	50 38	—
1̄01 010	11	89 48 — 90 21	90 1	90 0
101 · 210	13	49 52 — 50 35	50 12	—
210 11̄1	10	32 19 — 33 1	32 43	32 44
11̄1 · 10̄1	11	96 52 — 97 15	97 4	—
001 1̄11	2	68 17 — 68 25	68 21	68 13
1̄11 00̄1	2	111 31 — 111 47	111 39	111 47

45 *Toluenepasasulphanilide*, CH₃.C₆H₄ SO₂.NH C₆H₅

System . Monosymmetric

Axial ratios · a b . $c = 1·5424$ 1 0 8980.　$\beta = 99°\ 11'$

Habit   Well-formed crystals separate from a solution in ethylic acetate but the faces are frequently pitted   The most prominent faces are the two of the form {100} and the four of the form {$\bar{1}$11}   {101} and {110} always   appear as   triangular truncations and {$\bar{1}$01} appears occasionally (fig 33)

No definite cleavage could be detected.

Angle	No of observations	Limits	Mean	Calculated
$\bar{1}$00 101	16	126° 21′—127° 0′	126° 41′	126° 41′
$\bar{1}$00 $\bar{1}$01	3	66 40 — 67 15	66 56	66 49
101 101	3	59 32 — 59 48	59 42	59 51
101 100	15	53 2 — 53 36	53 19	—
$\bar{1}$11 $\bar{1}$$\bar{1}$1	15	78 52 — 79 26	79 5	—
$\bar{1}$11 11$\bar{1}$	13	100 36 —101 21	100 54	100 55
$\bar{1}$00 $\bar{1}$11	24	72 3 — 72 37	72 20	—
$\bar{1}$11 : 100	24	107 26 —107 54	107 40	107 40
100 110	7	56 34 — 57 17	56 55	56 51
10$\bar{1}$ $\bar{1}$11	6	112 31 —112 46	112 40	112 47
$\bar{1}$11 101	7	67 5 — 67 31	67 18	67 1d

46. Benzenesulphometaxylidide, $C_6H_5.SO_2 NH C_6H_3(CH_3)_2$

System   Monosymmetric.

Axial ratios   a b c = 0 7357 1 1 3484.   β = 97° 25′

Habit   Crystallised from acetone in prisms, the sides of the prisms consisting of the forms {010} and {012}, the form {$\bar{1}$01} being well developed at the prism ends (fig 34).

Forms present   b{010}, s{$\bar{1}$01}, p{012}, o{111}, x{$\bar{1}$21} and r{101}, the last form being always imperfectly developed

There is an imperfect cleavage parallel to s{$\bar{1}$01}

Angle	No of observations	Limits	Mean	Calculated
010 012	26	55° 45′- 56° 44′	56° 14′	—
012 0$\bar{1}$2	9	66 57 — 67 40	67 21	67° 32′
012 01$\bar{2}$	11	112 2 - 113 29	112 32	112 28
010 $\bar{1}$11	15	55 33 - 56 13	55 51	—
$\bar{1}$11 101	15	33 54 — 34 32	34 6	34 9
$\bar{1}$11 $\bar{1}$21	4	19 10 — 19 50	19 28	19 27
010 $\bar{1}$01	13	89 46 — 90 28	90 0	90 0
$\bar{1}$01 012	13	70 51 — 71 34	71 13	—
012 10$\bar{1}$	11	108 36 —109 5	108 44	108 47
101 10$\bar{1}$	1	57° 11′	57 11	57 1
012 $\bar{1}$11	2	54 41 — 55 8	54 54	54 40

47 Benzenesulphoparaxylidide, $C_6H_5.SO_2.NH C_6H_3(CH_3)_2$.

System   Monosymmetric

Axial ratios   a b c = 1 7644 1 1 2344.   β = 101° 56′

Habit   Crystallises from acetone in beautiful prisms, elongated in the direction of the c axis.

Forms present   a{100}, m{110}, s{$\bar{1}$01}, c{001}, o{$\bar{1}$11}, and occasionally r{101}.

No definite cleavage was detected.

Angle	No. of observations	Limits			Mean		Calculated	
100 101	12	63°	0' —	63° 27'	63°	14'	63°	16'
101 : 001	12	38	34 —	38 54	38	41	38	40
100 001	18	101	48 —	102 4	101	56	101	56
001 101	2	30	47 —	30 54	30	51	30	53
101 100	2	47	5 —	47 11	47	8	47	11
001 : 100	15	77	58 —	78 11	78	4	—	
101 111	20	47	31 —	48 8	47	47	—	
111 111	20	84	15 —	84 34	84	25	84	25
001 111	21	58	12 —	58 31	58	20	58	22
111 110	24	87	24 —	87 50	37	39	87	35
110 001	22	83	48 —	84 18	84	3	—	
110 111	4	60	39 —	60 50	60	43	60	41
100 111	23	59	37 —	60 7	59	56	59	55
110 110	18	59	45 —	60 29	60	4	60	10

Fig. 32 —44 Benzenesulphoparatoluidide.   Fig 33 —45. Tolueneparasulphanilide.

Fig. 34.—46 Benzenesulphometa-
xylidide.

Fig. 35.—48. Tolueneparasulphonortho-
toluidide.

48   *Tolueneparasulphonorthotoluidide*, $CH_3 C_6H_4 SO_2 NH C_6H_4 CH_3$

System   Orthorhombic

Axial ratios a b $c = 0.7725$: 1 : 0.9404

Habit   Crystallises beautifully from acetone or ethylic acetate in massive tables (fig 35)

Forms present $a\{100\}$, $b\{010\}$, $c\{001\}$, $o\{111\}$, $z\{121\}$

There is a perfect cleavage parallel to $b\{010\}$

Angle	No of observations	Limits	Mean	Calculated
010 121	25	39° 41'—40° 10'	39° 57'	39° 57'
121 111	23	18 57 —19 46	19 13	19 13
010 111	28	58 48 59 38	59 10	
111 1Ī1	9	61 21—61 54	61 89	61 40
100 111	26	48 12—48 40	48 26	—
111 Ī11	13	82 59 - 83 20	83 7	83 8
001 111	5	56 58 -57 5	57 2	56 59
111 11Ī	2	65 49—66 1	65 55	66 2
100 121	8	59 59 60 34	60 15	60 15
121 Ī21	1	59° 28'	59 28	59 30
001 : 121	17	65° 37'—66° 15'	65 56	65 57
121 12Ī	6	47 52 - 48 16	48 8	48 6

49   *Tolueneparasulphoparatoluidide*, $CH_3 C_6H_4 SO_2.NH C_6H_4 CH_3$

System   Anorthic

Axial ratios a b $c = 1.0525$: 1 : 0.9830 $\alpha = 74° 52'$, $\beta = 77° 3'$, $\gamma = 88° 25'$

Habit   Crystallises well from acetone in massive truncated prisms

Forms present $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $o\{111\}$

Cleavage good, parallel to $c\{001\}$

Angle	No of observations	Limits	Mean	Calculated
Ī00 ĪĪ0	3	45° 15' – 45° 48'	45° 31'	45° 44'
ĪĪ0 0Ī0	8	42 18 42 43	42 30	42 23
0Ī0 1Ī0	8	43 56 - 44 38	44 14	44 9
1Ī0 100	3	47 25 - 48 2	47 49	47 44
Ī00 0Ī0	9	87 49 - 88 21	88 7	—
0Ī0 100	9	91 31 — 92 17	91 52	91 53
Ī00 Ī01	13	54 48 — 55 45	55 12	—
Ī00 001	12	102 45 103 25	103 0	—
Ī01 001	15	47 34 47 58	47 46	47 48
001 100	12	76 23 — 77 30	77 0	77 0
0Ī0 ĪĪ1	14	57 40 — 58 22	58 2	—
0Ī0 Ī01	14	100 44 —101 34	101 17	—
Ī11 Ī01	12	42 58 — 43 38	43 13	43 15
Ī01 010	9	78 32 — 78 54	78 41	78 43
0Ī0 001	2	105 4 —105 13	105 8	105 11
001 010	2	74 47 — 74 56	74 51	74 49
ĪĪ0 ĪĪ1	6	43 3 — 43 35	43 15	43 18
Ī11 001	5	66 18 — 66 30	66 24	66 32
001 110	5	69 44 — 70 26	70 8	70 10

50 *Benzenesulphomethylanilide,* $C_6H_5 SO_2 N(CH_3).C_6H_5$

The axial ratios of this compound deduced by Brugnatelli[*] are

$$a \quad b \quad c = 2\,6965 \quad 1 \quad 3\,8618 \quad \beta = 79°\,45'$$

System Monosymmetric

Axial ratios $a \quad b \quad c = 2\,6940 \quad 1 \quad 1\,9302 \quad \beta = 100\,15'$

Habit Crystallised from acetone in massive colourless plates or prisms (fig 36)
Brugnatelli grew his crystals from ethylic acetate

Forms present $a\{100\}, c\{001\}, m\{110\}, s\{201\}, p\{20\bar{1}\}, o\{111\}, x\{11\bar{1}\}$

Cleavage parallel to $\{001\}$, not very good

Angle		No of observations	Limits				Mean		Calculated	
001	$\bar{1}11$	20	66°	34'—66°	52'		66°	42'	—	
$\bar{1}11$	$\bar{1}10$	13	26	43 —27	8		26	54	—	
$\bar{1}10$	$\bar{1}1\bar{1}$	12	25	27 —25	45		25	34	25°	30'
$1\bar{1}1$	$00\bar{1}$	18	60	39 —61	8		60	52	60	54
100	110	18	69	13 —69	34		69	20	—	
110	$\bar{1}10$	10	41	11 —41	34		41	22	41	20
$00\bar{1}$	$20\bar{1}$	9	61	48 —62	10		62	0	62	9
$20\bar{1}$	201	5	69	0 —69	46		69	20	69	31
201	001	6	48	9 —48	46		48	24	48	20
$20\bar{1}$	$\bar{1}11$	2	61	53 62	18		62	6	62	8
$\bar{1}11$	110	4	43	55 —44	16		44	4	44	0
110	$20\bar{1}$	2	73	41 —73	51		73	40	73	52
100	$\bar{1}11$	2	75	34 —75	57		75	40	75	52
$\bar{1}11$	$11\bar{1}$	2	36	51 —37	20		37	6	36	49
111	100	2	67	4 —67	9		67	6	67	19

Fig. 36.—50. Benzenesulphomethylanilide   Fig 37 —52 Benzeneparadisulphanilide

51 *Benzenemetadisulphanilide,* $C_6H_4(SO_2.NH Ph)_2$

System Monosymmetric

Axial ratios $a \quad b \quad c = 0\,497 \quad 1 \quad 0\,772 \quad \beta = 86°\,24'$

Forms observed $a\{100\}, b\{010\}, m\{110\}, r\{101\}, s\{\bar{1}01\}, o\{111\}, w\{\bar{1}11\}$

Angle	No of observations	Limits	Mean	Calculated
010 110	27	51° 27′ –52° 41′	52° 2′	52° 21′
100 110	21	37 14 —38 25	37 50	37 39
111 : 010	8	66 26 —67 13	66 45	—
101 111	13	22 26 -23 44	23 16	23 15
111 010	23	67 10 —68 58	67 55	—
101 111	22	21 16 —23 17	22 5	22 5
101 101	9	65 11 -66 13	65 33	—
100 101	4	59 1 —60 10	59 24	59 46
101 100	5	54 29 55 31	54 58	54 41

The crystals did not give good reflections, the faces soon becoming dull owing to change into a stable form

52 *Benzeneparadisulphanilide*, $C_6H_4(SO_2.NH\ C_6H_5)_2$

This compound crystallises from acetone in rather massive prisms (fig 37)

System Monosymmetric.

Axial ratios $a\ b\ c = 0\,4645\ 1\ 0\,1935\ \beta = 93°\ 41\frac{1}{2}′$

Forms present $b\{010\}, r\{101\}, n\{210\}, o\{\overline{1}11\}$.

There is a perfect cleavage parallel to $\{010\}$

Angle	No of observations	Limits	Mean	Calculated
210 210	13	25° 41′ —26° 23′	25° 59′	26° 6′
210 010	14	76 23 – 77 35	77 1	76 57
111 111	15	20 25 —20 57	20 41	—
111 010	24	79 9 —80 3	79 38	79 39½
101 : 111	21	45 49 —46 30	46 4½	—
111 210	21	68 32 -69 32	68 55½	—
210 101	22	64 28 —65 23	64 59	65 0

Acetanilides

Nos. 53–62 —These were prepared and measured by C T R. Wilson One of the most interesting results of this work is the observation that butyranilide exists in two forms—an orthorhombic and a tetragonal—and that these may be caused to pass over into one another reversibly by raising or lowering the temperature, the change involving an alteration in the angles which may be followed on the goniometer, no other obvious change takes place in the crystal.

53. *Propionanilide* crystallises from benzene in colourless thin plates or flattened needles, the dominant form being $o\{001\}$, other forms are $a\{100\}$ and $o\{111\}$

System Orthorhombic.

Axial ratios $a\ b\ c = 1\,0428\ 1.2\,1655$

There is a cleavage parallel to $a\{100\}$

Angle	Observed	Calculated
001 111	71° 34′	—
100 111	48 58	—
111 111	82 7	82° 4′

54 *Butyranilide* was originally measured by Otten,[*] who described it as tetragonal, $a\ c = 1\ 1\ 4836$ The optical properties of the crystals examined by him, however, were anomalous, as they sometimes indicated tetragonal, sometimes orthorhombic symmetry

This behaviour is due to the fact that the compound is dimorphous , when crystallised at a temperature above 14–18° C, it separates in orthorhombic forms , if kept at a lower temperature these crystals slowly change into a tetragonal form, the change being accompanied by the gradual equalisation of certain angles upon the crystal which are unequal in the orthorhombic form but equal in the more highly symmetrical tetragonal form. The observations recorded in the following table are typical of many that were made showing the passage from the orthorhombic to the tetragonal form, in which the two angles measured are the same —

Time	Angle			
	111 $\bar{1}$11		111 11$\bar{1}$	
days				
0	76°	44¼′	80°	35′
48	77	35	79	59
65	79	40	80	1
85	79	46	79	47

By crystallising the substance at lower temperatures, 8–11° C, tetragonal crystals can be obtained which become orthorhombic when kept at higher temperatures, although this change is slower than that in the opposite direction The changes can also be followed by optical methods

The most probable values of the axial ratios in the case of the orthorhombic form are

$$a\quad b\quad c = 0\ 7221\quad 1\quad 0\ 6894$$

These were calculated from the angles

$$111\quad \bar{1}11 = 76°\ 20',$$
$$111\quad 11\bar{1} = 80°\ 40'$$

The axial ratios of the tetragonal form are—

$$a\quad b\quad c = 0\ 6652\quad 1\quad 0\ 6652,$$
$$\text{or}\quad a\quad c = 1\quad 1\ 5033$$

Angle	No of observations	Mean
111 11$\bar{1}$	23	79° 35′

55 *Parabromoformanilide* forms large colourless crystals from solution in alcohol, acetone or ethylic acetate

System . Orthorhombic.

Axial ratios . $a\quad b\quad c = 1{\cdot}1028\quad 1\ {\cdot}\ 1\ 4100$

Forms observed $a\{100\}$, $b\{010\}$, $c\{001\}$, $o\{111\}$ and rarely $s\{112\}$

The dominant form is $\{111\}$

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[*] 'Zeit. Kryst. Min.,' vol 17, p. 391.

A very perfect cleavage was observed parallel to $a\{100\}$ The optic axial plane is parallel to $c\{001\}$, the optic axial angle is large, the obtuse bisectrix being perpendicular to $a\{100\}$

Angle	No of observations	Limits	Mean	Calculated
010 111	14	48° 50'—49° 10'	48° 59'	
111 001	19	61 55 —62 35	62 20½	—
111 11Ī	9	54 55 —55 32	55 17	55° 19'
112 001	9	43 33 —43 44	43 38	43 39½
111 1Ī1	10	81 43 —82 41	82 1	82 2
111 112	5	18 36 —18 58	18 46	18 41

Propylacetanilide is described by Duparc and Le Royer[*] as monosymmetric,

$$a \quad b \quad c = 1\ 3264 \quad 1 \quad ? \quad \beta = 101° 56'$$

If, however, the form $\{001\}$ be taken as $\{103\}$, the angle β becomes 90°, and it may then be regarded as pseudo-orthorhombic, the axial ratios being

$$a \quad b \quad c = 1\ 3264 \quad 1 \quad 0\ 8410$$

The substance then falls into line with its homologues, which are orthorhombic

56 *Parabromacetanilide* has been described by Mügge[†] and by Panebianco[‡] as monosymmetric.   Crystals were obtained from acetic acid solution, which were undoubtedly orthorhombic

The dominant forms present were $a\{100\}$ and $o\{111\}$.

System Orthorhombic

Axial ratios $a \quad b \quad c = 1\ 3904 \quad 1 \quad 0\ 7159$

Forms present . $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $n\{210\}$, $r\{101\}$, $q\{011\}$, $p\{301\}$, $o\{111\}$

A good cleavage was observed parallel to $p\{301\}$ and an imperfect one parallel to $a\{100\}$ The optic axial plane is parallel to $b\{010\}$

Angle	No of observations	Limits	Mean	Calculated
100 110	20	53° 47'—54° 32'	54° 16½'	—
100 111	27	67 5 —67 28	67 17	—
011 111	26	22 31 —22 55	22 42	22° 43'
110 111	18	48 22 —48 40	48 36	48 35
110 010	19	35 28 —36 10	35 42	35 43½
111 101	10	32 10 —32 40	32 33	32 29
111 1Ī1	7	82 32 —83 11	82 48	82 50
100 101	5	62 29 —62 58	62 42	62 45
100 301	4	32 20 —33 3	32 49	32 55
100 210	4	34 31 —35 1	34 47	34 48
011 110	5	61 36 —61 54	61 42	61 48
Ī11 301	4	42 48 —43 10	43 1	42 58

[*] 'Bull Soc Franc de Miner,' vol 14, p 54 (1891)

[†] 'Zeit Kryst. Min ,' vol. 4, p 335

[‡] 'Zeit Kryst Min ,' vol 4, p 393

57 *Parabromopropionanilide* separates from solution in ethylic acetate in large colourless crystals.

System   Orthorhombic

Axial ratios a b $c = 0\,4465$ 1 $0\,8948$

Forms observed $a\{100\}$, $b\{010\}$, $m\{110\}$, $q\{011\}$

There is a fair cleavage parallel to $a\{100\}$ The optic axial plane is parallel to $c\{001\}$, the optic axial angle is large and the a axis the acute bisectrix

Angle	No of observations	Limits	Mean	Calculated
100 110	24	23° 56′—24° 20′	24° 4′	—
110 011	20	74 4 —74 33	74 13½	—
010 011	27	47 56 —48 33	48 11⅓	48° 10⅓′
011 0Ī1	18	88 10 —83 54	83 37	83 39
010 110	18	65 21 —66 24	65 58	65 56

58 *Parabromomethylacetanilide* separates in large colourless crystals from alcohol, acetone or ethylic acetate   The forms $a\{100\}$, $c\{001\}$ and $m\{110\}$ are generally about equally developed $r\{101\}$ and $q\{011\}$ do not always appear

System   Monosymmetric

Axial ratios a b $c = 1\,5546$ 1 $0\,9719$. $\beta = 109°\,53'$

Forms observed $a\{100\}$, $c\{001\}$, $m\{110\}$, $r\{101\}$, $q\{011\}$

There is a very perfect cleavage parallel to $c\{001\}$ The plane of symmetry is the optic axial plane

Angle	No of observations	Limits	Mean	Calculated
100 110	40	55° 19′—55° 57′	55° 39′	—
001 110	35	78 49 —79 2	78 57	—
101 100	29	44 3 —44 41	44 16½	—
100 001	28	70 0 —70 22	70 7	70° 9′
001 011	19	42 7 —42 53	42 28	42 26

59 2 4 *Chlorobromacetanilide* (S S Napper).—It separates from solution in acetone or ethylic acetate in colourless monosymmetric crystals in which $a\{100\}$ is the dominant form.

System : Monosymmetric

Axial ratios a b $c = 0\,8144$ 1 $0\,6722$. $\beta = 76°\,55'$

Forms observed $a\{100\}$, $m\{110\}$, $q\{011\}$

There is a perfect cleavage parallel to $a\{100\}$ The optic axial plane is perpendicular to the plane of symmetry and the double refraction is negative

Angle	No of observations	Limits	Mean	Calculated
110 011	51	60° 32′—60° 59′	60° 44′	—
100 110	56	32 46 —33 29	33 12	—
011 0Ī1	44	76 35 —77 14	76 53	—
100 011	48	79 32 —80 18	79 51	79° 47′
011 Ī10	47	78 31 —79 13	78 58	78 56

60 2 4 *Bromochloracetanilide* may be crystallised from either acetone or ethylic acetate

System Monosymmetric

Axial ratios *a* : *b* : *c* = 0 8214 : 1 : 0 7074 β = 77° 46'.

Forms observed *a*{100}, *m*{110}, *q*{011}

The cleavage and optical properties are the same as for 2 4 chlorobromacetanilide

Angle	No of observations	Limits		Mean	Calculated
011 0$\bar{1}$1	41	77° 4'	77° 48'	77° 30½'	
100 110	54	34 18 —	34 57	34 19	
110 011	32	60 21 —	60 54	60 31	
011 $\bar{1}$10	29	77 6 —	77 25	77 19	77° 18'
100 011	25	80 8 -	80 53	80 30	80 28

61 *Parachloracetanilide* has been described by Fels* since the measurements here recorded were completed   Good crystals, belonging to the hemimorphic orthorhombic system, are obtained from solutions in ethylic acetate, acetic acid, or chloroform   The dominant forms are *a*{100} and *b*{010} , frequently {110} and {210} do not appear   The observation of Fels that the forms {101} and {111} appear at both ends of the *c* axis has not been confirmed, the former being found only at the positive end and the latter at the negative   The crystals are strongly pyroelectric

System Orthorhombic hemimorphic

Axial ratios *a* : *b* : *c* = 1 3263 : 1 : 0 6804

Forms observed *a*{100}, *b*{010}, *m*{110}, *n*{210}, *r*{101}, *o*{11$\bar{1}$}

There are cleavages parallel to {100} and {001}

Angle	No of observations	Limits		Mean	Calculated	Fels
11$\bar{1}$ 010	22	58° 27'	59° 9'	58° 49'	—	58° 37'
210 010	28	56 12 —	56 45	56 27	—	56 17
210 100	15	33 18 —	33 53	33 35	33° 33'	33 43
010 110	8	36 47 -	37 11	37 1	37 1	36 50¼
210 110	11	19 3 —	19 28	19 14½	19 26	19 26¼
11$\bar{1}$ 110	2	—		49 30	49 34½	—
11$\bar{1}$ 1$\bar{1}$$\bar{1}$	7	62 17 —	62 39	62 27	62 22	62 46
100 101	5	62 32 —	63 18	62 53	62 50	62 48½
210 2$\bar{1}$0	13	66 53 —	67 37	67 10	67 6	67 26

62 *Parabromethylacetanilide* separates from carbon bisulphide solution in orange coloured crystals

System Monosymmetric.

Axial ratios *a* : *b* : *c* = 1 4063 : 1 : 1 5686   β = 95° 35'.

Forms present *a*{100}, *c*{001}, *m*{110}, *r*{$\bar{1}$01}, *p*{$\bar{1}$02}

There is a good cleavage parallel to *c*{001}

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* 'Zeit Kryst Min,' vol. 32, p 386

Angle	No. of observations	Limits		Mean	Calculated
100 $\bar{1}$01	22	44° 10'—44°	59'	44° 21'	—
100 110	14	54 10 —54	40	54 27	—
$\bar{1}$01 : 001	0	51 5 —51	24	51 14	—
001 $\bar{1}$02	7	30 13 —30	44	30 28	30° 24$\frac{1}{2}$'
$\bar{1}$02 : $\bar{1}$01	5	19 55 —20	7	20 1	19 49$\frac{1}{2}$
100 001	17	84 14 —84	44	84 24$\frac{1}{2}$	84 25

REFERENCES TO ANILIDES

Formanilide   Wheeler, Smith, and Warren, 'Am. Chem J,' vol 19, p. 757 (1897)

Acetanilide   Bücking, 'Zeit f Kryst und Min,' vol 1, p 304.

Methylacetanilide   Duparc and Le Royer, 'Bull Soc Franc de Miner,' vol 14, p 54 (1891).

Ethylacetanilide   E Wickel, 'Zeit. f Kryst. und Min,' vol 11, p 81

p-Iodoacetanilide   Fels, 'Zeit. f Kryst und Min,' vol 32, p. 386

2 4 Dichloracetanilide   Keith, 'Neu Jahrb f Min,' vol 6, p 193 (1889).

2 4 Dibromacetanilide   Mügge, 'Zeit. f Kryst. und Min,' vol 4, p. 335

The Origin of Thermal Ionisation from Carbon.

By O. W. Richardson, M.A, D Sc, F.R.S

In the 'Proceedings'[*] Dr J N Pring describes interesting experiments designed to throw light on the origin of thermal ionisation from carbon. These experiments form a continuation of earlier experiments along similar lines by J N Pring and A Parker[†] In commenting on the results of the earlier work, Dr Pring says :—

" It has been shown by the present writer, in conjunction with A Parker, that the ionisation which is produced by carbon at high temperatures, and in presence of gases at low pressures, is reduced to a much smaller order of magnitude by eliminating impurities from the carbon, and by exhausting to a high degree the containing vessel

" *The results throw considerable doubt on the whole basis of the theory of electronic emission from incandescent solids*

" According to this theory,[‡] the ionisation produced by elements at high temperatures is due to the escape of free electrons, which pass into the surrounding space on account of the kinetic energy acquired at the high temperature

" It was shown, however, in the above work that in the case of carbon this ionisation *is probably related to some chemical action* or some intermediate effect *exerted by the gas in contact with the solid*."

In the summary and conclusions at the end of the later paper Dr. Pring states :—

" *It is clear from these results that the thermal ionisation ordinarily observed with carbon is to be attributed to chemical reaction between the carbon and the surrounding gas*

" While it is difficult to prove definitely that there is no electronic emission from the heated carbon itself, *it is obvious that it is exceedingly small compared with ionisation which can be attributed to ordinary chemical change*"

The object of the present note is to point out certain conditions affecting the arrangement of apparatus used by these authors which make it quite certain, in the opinion of the present writer, that none of the statements

[*] 'Roy Soc Proc,' A, vol 89, p. 344 (1913)

[†] 'Phil Mag,' vol 23, p 199 (1912)

"[‡] Richardson, 'Phil Trans,' 1903, A, vol 201, p. 497, 'Phil Mag,' 1912, vol. 24 pp. 737–744, *ibid*, 1913, vol 26, p. 345 "

italicised above can be regarded as a valid inference from the results of the experiments in question. In the discussion which follows, the numerical values refer to the apparatus figured in Dr Pring's paper in the ' Proceedings,' although the objections apply with at least equal force to the arrangement used in the earlier experiments of Pring and Parker

The apparatus used in these researches differs in two very important respects from that which has been employed by other workers in the same field. The size of the hot solid is very much greater than usual, and the current required to heat it is correspondingly bigger Under these conditions the effect of the magnetic field arising from the heating current is quite important, and when this is taken into account the phenomena recorded can certainly not be said to contravene the requirements of the ordinary theory of electronic emission

In the experiments under consideration a hollow carbon rod, 0 5 cm in diameter and 8 cm long, was the source of negative emission. To heat it to a temperature of 1850° a current of 80 ampères was required The leakage from the hot rod to a small disc, placed 8 cm. away from the rod in the equatorial plane, was measured Potential differences up to 220 volts could be applied between the rod and the insulated disc

The geometry of this arrangement is so complex that it is impossible to make definite numerical statements as to the distribution of the electric intensity It will, however, be sufficient for our purpose to consider a somewhat similar system, in which the disc is replaced by a cylindrical conducting surface coaxial with the hot rod The electric intensity is then radial and, at a distance r from the axis, is, in electromagnetic units,

$$R = \frac{V_1 \times 10^8}{r(\log b - \log a)}, \qquad (1)$$

where V_1 is the potential difference in volts between the rod and the cylinder, a is the radius of the rod, and b the radius of the cylinder. The magnetic intensity H is in circles about the axis and, at a radial distance equal to r, is given by the equation

$$H = \frac{2i}{10r}, \qquad (2)$$

where i is the current through the rod in ampères. The motion of an electron starting with zero velocity at the surface of the rod is in planes containing the axis, under this system of forces It is determined by the equations

$$m\frac{\partial^2 r}{\partial t^2} = Re - He\frac{\partial z}{\partial t} \qquad . \qquad (3)$$

and

$$m\frac{\partial^2 z}{\partial t^2} = He\frac{\partial r}{\partial t}. \qquad (4)$$

These may be written

$$m \frac{\partial^2 r}{\partial t^2} = \frac{Ae}{r} - \frac{Be}{r} \cdot \frac{\partial z}{\partial t} \qquad (5)$$

and

$$m \frac{\partial^2 z}{\partial t^2} = \frac{Be}{r} \cdot \frac{\partial r}{\partial t} \qquad (6)$$

m is the mass of an electron, z is the distance parallel to the axis

$$A = \frac{V_1 \times 10^8}{\log b - \log a}, \quad \text{and} \quad B = \frac{\imath}{5} \qquad (7)$$

From (6)

$$\frac{\partial z}{\partial t} = \frac{Be}{m} \log \frac{r}{a}, \qquad (8)$$

if $\partial z / \partial t = 0$, when $r = a$

After elimination of z from (5) by means of (8), the first integral of (5) is seen to be

$$\left(\frac{\partial r}{\partial t}\right)^2 = \left(\frac{2}{m} \log \frac{r}{a}\right) \times \left(Ae - \frac{1}{2} \frac{B^2 e^2}{m} \log \frac{\imath}{a}\right) = \left(\frac{Be}{m} \log \frac{r}{a}\right)^2 \left(\frac{\partial r}{\partial z}\right)^2, \qquad (9)$$

subject to $\partial \imath / \partial t = 0$, when $r = a$.

It follows from (9) that the maximum distance r_m which an electron can travel away from the axis is given by

$$r_m = ae^{2mA/B^2 e} = ae^{(2V_1 \times 10^8 \times 25)/[\log (b/a) \times (e/m) \times \imath^2]}. \qquad (10)$$

In one of Dr. Pring's experiments the values of the quantities entering into the exponent were, at 1850°,

$$V_1 = 220, \quad b = 8, \quad a = 0.25, \quad \text{and} \quad \imath = 80$$

The value of e/m is 1.76×10^7 electromagnetic units, so that even under the relatively favourable conditions contemplated, the maximum distance which an electron could travel from the axis would be

$$r_m = 4.19 \text{ cm}$$

This distance increases rapidly as the heating current diminishes, so that when the heating current is 57 ampères the distance becomes about 62 cm., instead of 4.19 cm Thus, if the conditions which held during the experiment were exactly those contemplated in these calculations, the electrons would only be prevented from reaching the electrode with the largest heating currents which were used .

But the actual conditions, in the experiments referred to, are much less favourable to the escape of electrons than those which we have assumed. The collecting electrode was of comparatively small size, so that most of the potential fall would occur in its immediate neighbourhood and the electric field near the rod would be greatly weakened. Even so, the relatively strong

part of the field would be confined to the equatorial region, there would be very little near the ends. Moreover, the glass bulb would tend to acquire a negative charge, which would help to shield the rod from the field arising from the positively charged electrode. Finally, any electron which found itself in the region occupied by the relatively strong electrostatic field would quickly be deflected out of this region by the action of the magnetic field.

Thus, in the experiments with the larger currents, none of the emitted electrons would be able to travel a distance from the axis equal to half the distance of the collecting electrode, and very few would be able to travel away a distance comparable with this. Even with the (presumably) smaller heating currents employed at the lower temperatures, one cannot be certain that there ought to be any measurable leakage in these experiments arising from electronic emission. Conclusions drawn from these calculations are valid only at the very lowest pressures, when the amount of gas present is too small to affect either the nature of the ions or their motion.

It remains to consider whether it is necessary to attribute to chemical action the origin of the increased currents which are observed when traces of different gases are present. There are at least two ways in which the presence of a gaseous atmosphere would influence the number of ions collected by the positive electrode. The first of these is by the mechanical interference of the molecules with the motion of the ions through mutual collisions. This kind of effect would undoubtedly produce a large increase in the current received if the pressure were increased by very considerable amounts, but one would hardly expect it to be important at pressures below 0·005 mm, where the mean free path of an electron is comparable with 10 cm in the simpler gases. The second way is by direct combination of the electrons with the molecules and atoms of the surrounding gas. This would result in the formation of ions possessing masses of atomic magnitude and correspondingly smaller values of e/m. These ions would not be deviated appreciably by the magnetic fields, but would follow the lines of electric force fairly closely until they reached the positive electrode. This explanation of the nature of the currents observed by Dr Pring at very low pressures is supported by the order of comparative efficiency of the different gases, as well as by the large specific effects produced by such small quantities of gas. The order is, in fact, very much the same as that found by Sir J. J. Thomson[*] for the relative frequency of occurrence of the corresponding negatively charged atoms and molecules in the positive rays.

It may be well to add that the currents at the higher temperatures cannot be due simply to the emission of *electrons* from the hot carbon under the

[*] 'Roy. Soc. Proc.,' A, vol. 89, p. 1 (1913).

influence of chemical action, unless the nature or motion of the emitted electrons is modified subsequently in some such way as that outlined.   For the calculations given above have shown that such electrons would never reach the collecting electrode   In any event if chemical action were the determining factor one would rather expect the effect of carbon dioxide to be of a different order from that of any of the other gases investigated

It seems probable that chemical action does influence the phenomena under consideration in another way, and that the number of heavy ions formed is determined by a reaction between the electrons liberated from the carbon and the products of the action of the surrounding gas on the hot carbon   This is quite different from supposing that the electrons are emitted as a consequence of the action of the gases on the carbon   It may be that there is an emission of electrons from carbon which is stimulated directly by chemical action, but there is, so far as the writer is able to judge, no experimental evidence at present which would compel us to accept this as an established fact

The most important conclusions which would seem to follow from the foregoing discussion are —

1. In those of the experiments in question in which heating currents in the neighbourhood of 80 ampères were employed, and temperatures in the neighbourhood of 1800° C or higher were attained, none of the electrons emitted by the carbon would reach the collecting electrode, at the lowest pressures

2 Owing to the geometrical arrangement of the apparatus, which does not lend itself to exact calculation, it is impossible to say what proportion of the emitted electrons would reach the electrode when the smaller heating currents were used, at low pressures.   In any event, it cannot be said with certainty, judging from such data as are at present available, that the minimum currents observed by Dr Pring at 1200° C are smaller than those which would be called for by the ordinary thermionic theory   It is only the currents at the higher temperatures which seem definitely out of line, and the smallness of these is readily accounted for by the magnetic deflection

3 An increase of the observed currents with increasing gas pressure is to be expected on account of—

(*a*) The interference of the gas molecules with the motion of the electrons , and

(*b*) The combination of the electrons with atoms and molecules of the gases.

The large specific effects produced by traces of different gases seem to indicate that (*b*) may be an important factor

4 The experiments cannot be held either to prove that the emission of electrons from hot carbon is an immediate consequence of chemical action between the carbon and the surrounding gases or to invalidate those theories which regard this effect as a physical property of the hot solid.

The Magnetic Properties of Iron when Shielded from the Earth's Magnetism.

By Ernest Wilson

The primary object of the experiments described in this paper is to examine the magnetic properties of iron under small magnetic forces when shielded from the earth's magnetism In a previous paper[*] experiments were described in which these magnetic properties were examined at low forces, and hysteresis loops obtained at maximum values of the magnetic induction as low as 0 937. The specimen, which was of the same material as used in the present experiments, was exposed to the influence of the earth's magnetism, and it is this influence which has now been removed as far as possible.

The specimen is of ring form and is built up to an axial length of 38·8 cm. of stampings of an alloy of iron known as "Stalloy," containing 3 per cent of silicon. The internal and external diameters of each stamping are 7 6 and 12 75 cm respectively, and the thickness varies from 0 34 to 0 14 cm The secondary winding is next to the stampings and has 177 turns of copper wire 0 81 mm diameter insulated by cotton impregnated with paraffin The primary or magnetising winding has 10 turns of copper strip 19 mm wide and 0·13 mm thick covered with insulating tape

The shield is built up to a length of 47 cm of stampings of transformer iron 0·62 mm thick The internal and external diameters of each stamping are 30 5 and 40 6 cm. respectively. At each end are discs of soft iron 40·6 cm diameter which together with two square end plates make up an overall length of 56 cm The shield is firmly clamped by four bolts passing through

the end plates.   For the insertion of the primary and secondary windings a few of the stampings nearest to the end discs have a small piece cut away so as to form a narrow opening into the shield.

The specimen is supported symmetrically within the shield and their common axis is placed at right angles to the magnetic meridian

Throughout the experiments the ballistic galvanometer has been used When it was desired to demagnetise the specimen, an alternator was used whose wave-form is a smooth curve having a maximum ordinate somewhat larger than that of an equivalent sine curve, and the current was gradually reduced by variation of resistance until it was of the order 4×10^{-4} ampère, the alternator being finally allowed to come to rest with its excitation left on

In Table I will be found, for the respective experiments which are numbered, the magnetic induction B and in some cases the permeability μ corresponding to the given force H   In Table II will be found the figures obtained at the higher forces.   In Table III will be found the results obtained from the hysteresis loops.

Preliminary experiments were made when the specimen was inside the shield in the virgin state, that is to say, as received from the makers and in a demagnetised state, the maximum magnetic force impressed upon the specimen being 0 59 C.G S unit   At this stage it was discovered that the insulation of the secondary winding was defective, and this threw a criticism upon the experiments   It is necessary to mention this because the previous magnetic history of the specimen is important, and the results will be alluded to later   The specimen was re-wound, and the experiments made thereafter may be placed in the following order.

Experiment 1   Specimen out of shield and exposed to the influence of the earth's magnetism.   Hysteresis loops obtained.

Experiment 2   Specimen in shield   Hysteresis loops obtained after careful demagnetisation from a force of 0 59

Experiments 3, 4, 5, 6   Specimen in shield and showing how high permeability was produced

Experiments 6, 7, 8   Specimen in shield and showing the effect on permeability of allowing it to rest in a highly magnetised state

Experiments 9, 10, 11, 12: Specimen in shield and showing the effect of allowing it to rest in a less highly magnetised state.

Experiments 13, 14, 15, 16, 17. Specimen in shield and showing the effect of allowing it to rest in a demagnetised condition

Experiments 18, 19, 20 · Specimen in shield.   Hysteresis loops obtained after a moderate rest in demagnetised condition

I. *Permeability.*

Experiments 1, 2 : Before placing the specimen in the shield, Experiment 1 was made after demagnetisation from a force 0·3 at 52 complete periods per second For each of the forces mentioned in Table I a hysteresis loop was obtained, the details of which are given in Table III When in the shield the specimen was demagnetised from a force of 0·59, and Experiment 2 was made Hysteresis loops were again obtained for the same forces as in Experiment 1 The permeability curves 1, 2, are plotted in fig 1, and correspond to Experiments 1, 2, respectively For comparison, the curve of permeability obtained in the previous paper (*loc cit*) is also plotted This curve is somewhat higher than in Experiment 1, and in this connection it should be noted that the demagnetisation had been made from a much higher force than 0 59. Near the origin it differs in shape from those obtained in Experiments 1, 2

Experiments 3, 4, 5, 6, on the production of high permeability · Up to this point it should be noted that the highest force ever applied to the specimen has been 0 59, and, at the close of Experiment 2, the specimen was left magnetised as the result of a force 0 0935, and eight days elapsed before further experiments were made   At the end of this time a magnetising force of 0 8, due to a continuous current, was applied, reversed a few times, and removed   Such a force as 0 8 applied to a demagnetised specimen has, in ordinary magnetic testing, a degrading or polarising effect, that is, the magnetic induction corresponding to a given smaller force is then lower than it would have been had the iron been in a demagnetised state originally *   In the shield, however, the reverse is the case, the specimen having been previously exposed to the earth's magnetism, and not subjected to so high a force as 0·8. A comparison of the figures obtained in Experiments 2 and 3, Table I, shows the increase in the permeability at the low forces. A comparison of curves 2, 5, in fig 1 shows in the early stages how great is the increase in permeability caused by carefully demagnetising the polarised specimen

Experiment 6 was next made to investigate the effect on permeability at higher forces than those given in Table I. It is practically a continuation of Experiment 5 and the figures are given in Table II In fig 2 the curve 6 shows the result obtained, and, for the purpose of comparison, the values of the permeability obtained in the earlier paper (*loc. cit*). A maximum permeability of 5750 corresponding to a magnetic induction of 5500 is indicated, whereas the old experiments on the unshielded but

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* 'Roy. Soc. Proc.,' A, vol 83, p. 1 (1909)

carefully demagnetised specimen show a maximum of 4600 for a magnetic induction of 5000   In the case of a specimen of almost pure iron a permeability of 5480, corresponding to a magnetic induction of 9100, was obtained,* and this is a high value.

Experiments 6, 7, 8, deal with the effect of resting the specimen when in a magnetised condition   Experiment 7 was made immediately after Experi-
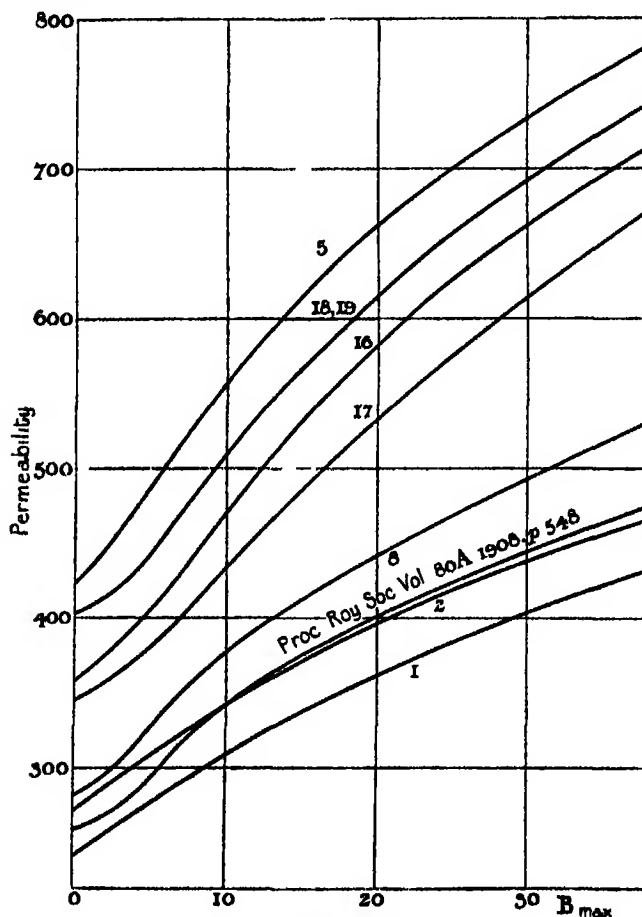
Fig 1.

ment 6 was completed, that is without demagnetising the specimen, and in Experiment 6 the force was taken up to 1·8   The result shows how greatly the permeability is affected in the earlier stages by the application of this previous force of 1 8   The specimen was again polarised by a force of 1·8 and left in this condition for about 18 hours.   Experiment 8 was then made

* 'Roy Soc Proc,' vol. 62, p 369.

and continued to the higher forces as before, and the figures are given in Table II   Curve 8, fig 1, shows how greatly the permeability is reduced in the early stages, and Curve 8, fig 2, shows the later stages.   It will be seen that for a magnetic induction of 5500 a permeability of 5900 is obtained, and this is even greater than that shown by Experiment 6 Curves 6, 8, cross one another at an induction of about 3500, and coincide when the induction is about 10,000.   The similarity of Curve 8 in fig 1 with that taken from the earlier paper is interesting.   In the one case we have the specimen carefully demagnetised and exposed to the earth's magnetism, in the other the specimen is polarised and shielded   It is worthy of note that when in the polarised condition of Experiments 7, 8, careful
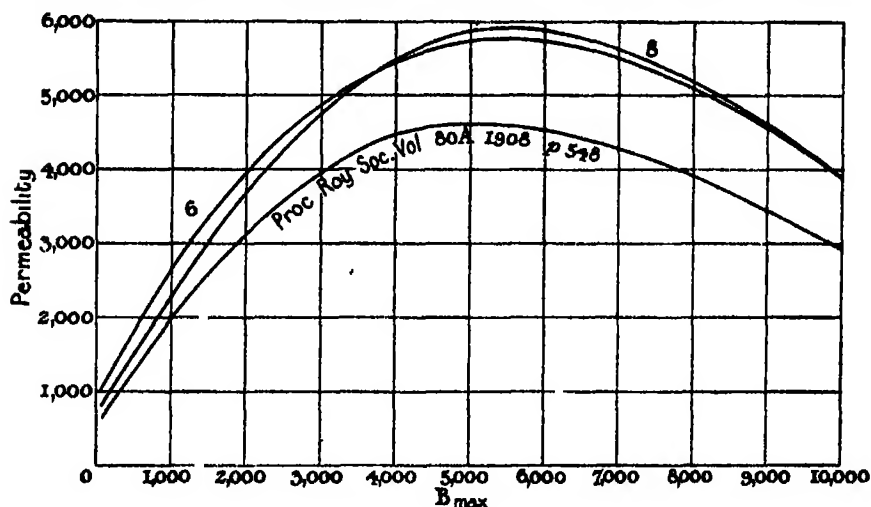
Fig 2

demagnetisation is required to restore maximum permeability at the lower forces.

Experiments 9, 10, 11, 12, show the effect of two periods of rest when the specimen is left polarised by the application of a force of 0 0935   It will be seen that when left the specimen tends to degrade itself or to experience a fall of permeability in the earlier stages, but it gets into a fairly stable state after a long enough interval. This will be apparent if Experiment 12 be compared with Experiment 16 of the next section.

Experiments 13, 14, 15, 16, 17, show the effect of resting in a carefully demagnetised condition for periods of 3, 18½, 48 hours and 13 days respectively.   The same (degrading) process is at work in the earlier stages, but after 48 hours' rest the specimen is more stable.   The continuation of Experiment 17 is given in Table II.   The points when plotted in fig. 2

Table I.—Permeability

Expt.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Maximum magnetic force H	Out of shield after demagnetisation from H = 0.5	In shield after demagnetisation from H = 0.49	In shield after polarisation at H = 0.5	In shield after demagnetisation from H = 1.5	In shield immediately after demagnetisation from H = 3.97	In shield 1½ hour after demagnetisation from H = 5	In shield immediately after polarisation at H = 1.5	In shield 18 hours after polarisation at H = 1.5	In shield after demagnetisation from H = 2.5	In shield 18 hours after polarisation at H = 0.093	In shield after demagnetisation from H = 1.5	In shield 48 hours after polarisation at H = 0.093	In shield after demagnetisation from H = 1.5	In shield 4 hours after demagnetisation from H = 5	In shield 18½ hours after demagnetisation from H = 1.5	In shield 48 hours after demagnetisation from H = 1.5	In shield 14 days after demagnetisation from H = 2.5	In shield 4½ hours after demagnetisation from H = 5	In shield 1½ hours after demagnetisation from H = 5
	B 0.204	B 0.248	B 0.296	B 0.340	μ 427 / B 0.362	B 0.344	μ 298 / B 0.253	μ 283 / B 0.240	B 0.362	B 0.317	B 0.362	B 0.302	B 0.341	B 0.338	B 0.311	B 0.306 / μ 361	B 0.294	B —	B 0.88
0.000048	0.412	0.463	0.600	0.680	429 / 0.721	0.666	299 / 0.502	283 / 0.476	0.729	0.632	0.717	0.632	0.718	0.673	0.631	0.612 / 364	0.586	—	—
0.00108	1.04	1.18	1.55	1.75	443 / 1.96	1.78	309 / 1.30	288 / 1.21	1.87	1.61	1.85	1.58	1.84	1.74	1.63	1.57 / 374	1.50	1.72	—
0.00420	2.13	2.44	3.26	3.74	472 / 3.96	3.74	316 / 2.66	273 / 2.48	3.94	3.40	3.90	3.26	3.91	3.63	3.40	3.26 / 387	3.06	3.50	—
0.00943	4.9	6.36	7.98	—	556 / 9.95	9.33	346 / 6.19	340 / 6.08	—	8.45	9.66	8.08	9.49	9.04	8.20	7.91 / 443	7.16	8.92	38.4
0.0179	17.2	19.6	36.8	36.3	791 / 36.2	37.7	447 / 29.2	456 / 22.7	38.2	35.1	37.7	34.0	37.8	36.5	34.8	34.4 / 644	31.1	—	38.4
0.0955	41.2	45.7	67.6	66.2	1000 / 93.7	91.8	557 / 50.2	542 / 52.5	91.0	86.8	89.8	85.4	89.7	88.3	86.4	85.6 / 915	83.6	—	88.3

Table II.—Permeability.

Experiment 6 continued			Experiment 8 continued			Experiment 17 continued		
Maximum H	Maximum B	Permeability, μ	Maximum H	Maximum B	Permeability, μ	Maximum H	Maximum B.	Permeability, μ.
0·0996	110	1100	0·100	62·2	619	0·118	126	1070
0·138	172	1250	0·140	98·9	706	0·219	324	1480
0·206	311	1510	0·208	172	827	0·292	537	1840
0·279	521	1870	0·281	284	1010	0·435	1310	3010
0·329	767	2330	—	—	—	0·583	2600	4460
0·411	1190	2900	0·411	848	2060	0·829	4730	5710
0·465	1600	3450	0·468	1286	2750	1·13	6430	5690
0·584	2660	4560	0·588	2560	4350	1·47	7780	5260
0·780	4310	5530	0·782	4410	5640	1·74	8510	4890
1·03	5900	5730	1·03	6080	5850			
1·32	7220	5470	1·31	7210	5510			
1·52	7830	5150	1·52	7910	5200			
1·81	8680	4790	1·80	8660	4810			

Table III —Hysteresis

No. of Experiment	Maximum H.	Maximum B	Ergs per cycle per cubic centimetre	Steinmetz index, β	Steinmetz constant, α	Permeability, μ	Coercive force, H_0	Residual magnetic induction, B_0
1	0·000499	0·117				235		
	0·000849	0·204				240		
	0·00168	0·412				246		
	0·00420	1·04	0·0000190	1·84	0·0000177	248	0·000062	0·018
	0·00843	2·15	0·0000723	2·92	0·00000774	255	0·00018	0·038
	0·0179	4·9	0·000801	2·36	0·0000188	274	0·00071	0·18
	0·0496	17·2	0·0155	2·10	0·0000396	347	0·00417	1·47
	0·0935	41·2	0·0974			441	0·01	4·55
2	0·00168	0·462				275		
	0·00420	1·18	0·0000175	1·62	0·0000134	281	0·000047	0·016
	0·00843	2·44	0·0000569*	3·30	0·0000030	289		
	0·0179	5·55	0·000861	2·41	0·0000139	310	0·00050	0·16
	0·0496	19·6	0·0181	2·04	0·0000419	395	0·0040	1·47
	0·0935	45·7	0·102			489	0·010	4·45
18 and 19	0·00168	0·68	0·0000310	2·47	0·00000808	405	0·000016	0·0068
	0·00420	1·72	0·0000806	3·00	0·00000602	410	0·000058	0·028
	0·00843	3·59	0·000279	2·58	0·0000103	426	0·00031	0·18
	0·0179	8·92	0·00291	2·18	0·0000278	498	0·0014	0·65
	0·0496	36·4	0·0583	2·13	0·0000278	734	0·0063	4·9
	0·0935	88·3	0·306	1·87	0·0000702	944	0·0138	14·0
20	0·191	287·0	2·1	2·01		1240	0·037	47·4
	0·418	1016·0	39·5			2430	0·170	454·0
	0·763	4840·0	449·0	1·68		5540	0·398	3160·0
	1·63	8210·0	1800·0	1·67		5070	0·531	6130·0

* It is probable that this value for the ergs is slightly too small. For some reason the curve is not so satisfactory as it should be, but it could not be repeated.

practically coincide with those of Curve 6   The rest of 13 days has produced the most noticeable effect at the lowei forces

[*Note added February* 26, 1914—A rest of six weeks in a demagnetised condition shows no further diminution in permeability than does the rest of 13 days]

II *Hysteiesis*

In the previous paper (*loc. cit*) when the stalloy specimen was exposed to the earth's magnetism, it appeared that the Steinmetz index increased from its ordinary value of 1 7 to 2 69, when the magnetic induction reached the value of 0 94   The present experiments show that after demagnetisation in or out of the shield the value of the index rises to a maximum in the neighbourhood of a magnetic induction of 3 and then diminishes   The preliminary experiments made when the specimen was in the virgin state bear out the same remark   The shape of the loops is well worthy of study The loops in fig 3 are selected from those taken in Experiments 18 and 19,

No of LOOP	H_{max}	B_{max}
1	0·0935	88 3
2	0·0179	8 92
3	0·00420	1 72
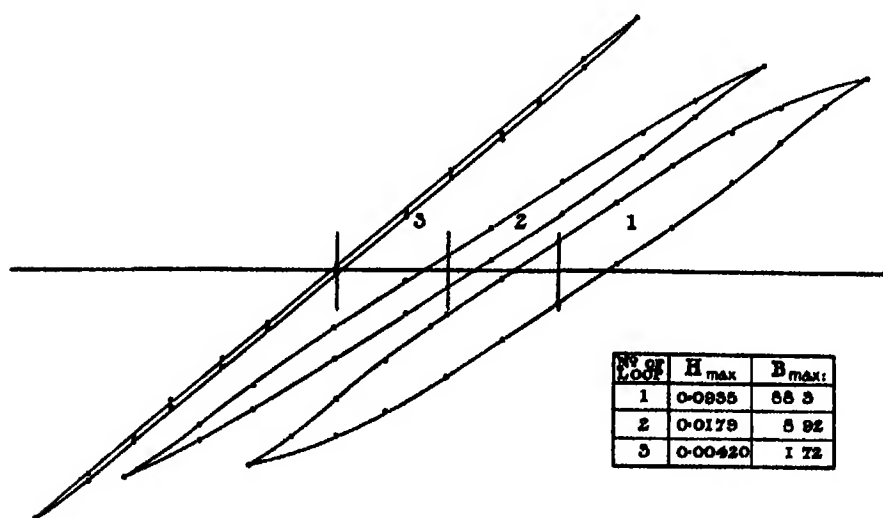
Fig 3.

and it will be seen that as the induction is reduced the shape is altered   The character of loop 1, for instance, when the maximum induction is 88·3, is more like that of the loop with which one is familiar in ordinary testing, but it has sides which for a short distance are practically parallel straight lines.   This is the beginning of a pronounced alteration in shape   Loop 2, fig. 3, shows this carried to a further stage   Loop 3 is remarkable in that its sides are practically two parallel straight lines, and the index has nearly

passed its maximum value   Reference should be made to an interesting paper on this subject by Dr W M Thornton [*]   The Steinmetz equation is that the ergs per cycle per cubic centimetre are equal to αB^{β}, where α and β are constants and B is the magnetic induction   The values of α and β are given in Table III   As to what would be the values of the index β if the experiments could be carried further cannot be said at present.

It should be mentioned that the coercive force has been taken from the point where the mean curve cuts the axis of H   It is well known that at this point on the curve the magnetic instability is such that tapping the specimen causes a change in the magnetic induction   When the force is varied from a positive or negative maximum to zero this instability in some cases asserts itself and would, if a mean curve were not drawn, indicate a somewhat smaller coercive force.

A few loops have been obtained as a continuation of Experiments 18 and 19 at the higher forces when the specimen was in a demagnetised condition and after a rest in that condition of one and a half days   The particulars are given in Table III, Experiment 20   By comparing them with the figures obtained in the earlier paper it will be seen, for instance, that for a magnetic induction of 8200, the ergs per cycle per cubic centimetre are less when in the shield in the ratio 1300/1688, and the permeability is greater in the ratio 5070/3850   The coercive force H_0 and the residual magnetic induction B_0 are less

The experiments throw light upon the early stages of the ordinary curve, which shows the relation between the coercive force and the intensity of magnetisation , it resembles the curve connecting the functions H and B of magnetic materials

Conclusion

The experiments show that the earth's magnetism may seriously affect the magnetisability of iron   Comparing the results obtained in these experiments when stalloy (in ring form) is magnetised and then carefully demagnetised whilst shielded from the earth's magnetism, with the results of similar experiments made on the same material in a carefully demagnetised condition but exposed to the earth's magnetism, the ratio of the permeabilities has a maximum of 1 79 when the magnetic induction has a value 172, and the ratio of the maximum permeabilities is 1·24   A maximum permeability of 5900 was obtained when the specimen was shielded and magnetised by a previous force of 1·8 C G.S. units, and this is 1 28 times the maximum permeability obtained from the demagnetised and exposed specimen.   The

dissipation of energy by magnetic hysteresis for a given magnetic induction is less when the stalloy is in the shield and demagnetised than when it is first demagnetised and then exposed to the earth's magnetism   The Steinmetz index, after rising to a maximum of about 3 for a force of about 0·008 C G.S unit, begins to diminish as the force is reduced, and at about this point the hysteresis loops begin to experience a change in shape, becoming practically straight parallel lines

[*Note added March* 10, 1914 — As was mentioned during the reading of the paper, the high permeability has persisted since the specimen was taken out of the shield on February 17, 1914.   Experiments which are just completed show that it still exists]

The Boiling-point of Sulphur on the Thermodynamic Scale.

By N. EUMORFOPOULOS, B Sc , Fellow of University College, London

The experiments described in this paper were carried out with the constant-pressure gas thermometer The form of the apparatus has been already given in some detail in a previous paper,[*] the results of which were not regarded as final owing to the alteration in volume of the glass bulb The latter was, therefore, changed for one of fused silica, and, of course, the compensation tubes were likewise of silica It is unnecessary to repeat all the details given in the previous communication, any change will be mentioned here , it can be assumed that the mode of experiment has remained the same in all other particulars To avoid continual references back to this paper, figs 1 and 2 are here repeated Fig 1 represents the bulb and expansion vessel, while fig 2 shows the two gauges (the mercury and oil gauges), it
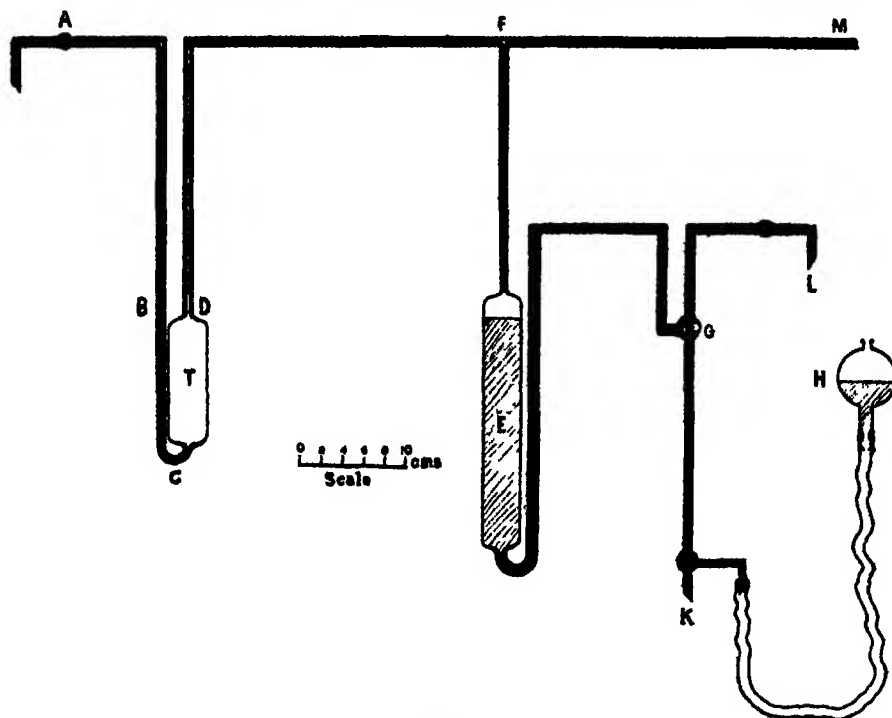
FIG 1

[*] N. Eumorfopoulos, 'Roy Soc Proc.,' A, vol. 61, p 339 (1908)

should be added that the oil-gauge tap has since been changed for the tap shown in fig 5 of the present paper

The silica bulb and connecting tubes are drawn roughly to scale in fig 3

Two silica bulbs have been used of practically the same volume, the one has the form shown in the figure, in the other, the bulb is connected immediately to the tube B, the capillary tube D being continued down to C
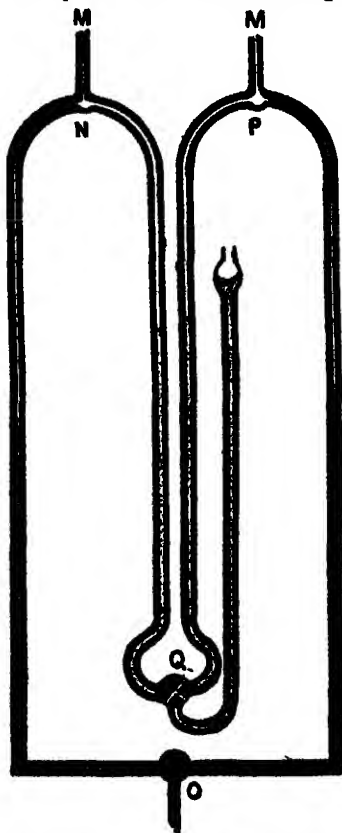
Fig 2
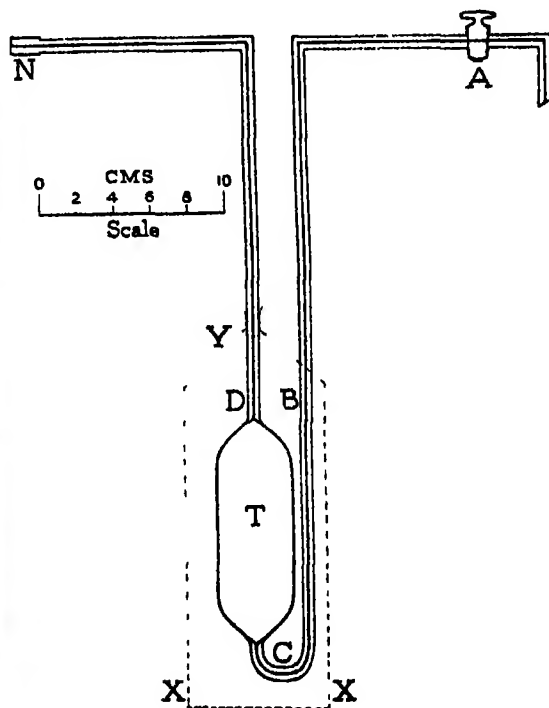
Fig 3

The compensation tubes are similar to the above, except that the bulb is missing, the capillary tube passing directly across from B to D   The silica apparatus was made by the Silica Syndicate, the capillary tubes were selected from a large number, so as to obtain proper compensation.   How far this has been successful will be seen from the following table —

	Bulb 1	Bulb 2	Compensation tubes.
Tube B	0 1103 grm./cm	0 1048 grm /cm	0 1246 grm./cm.
„ D	0 0266 „	0 0298 „	0 0176 „
	0 1369 „	0 1346 „	0 1422 „

(All volumes are given in grammes of mercury at 0° C)

To join the end N of the silica tube to the rest of the apparatus, a little Prout's glue was smeared over the silica, the latter gently warmed and pressed into position against the glass tube to the left of F (fig 1), over this junction was slipped a glass sleeve a few centimetres long, leaving a clearance of about a millimetre, into which was poured cement   This cement was made according to Faraday's recipe, but a larger quantity of beeswax was added than is given in the directions   Finally, the ends of the sleeve were covered with true Faraday cement   It was, however, found necessary to introduce mercury into the capillary tube while carrying out the above operation, otherwise the wax dropped into the tube and completely closed it The tubes were then evacuated, and the cement at the two open ends partially melted, so that the wax could be sucked in, if the Prout's glue did not hold properly

Pressure Coefficient of the Silica Bulb

This was measured with the following results   With the bulb full of mercury, an increase of pressure of 1 cm of mercury produced an apparent change of volume —

$$\begin{aligned} \text{At} \quad &0° \text{ of } 0\,00124 \text{ grm} \\ \text{„} \quad &100° \text{ „ } 0\,00126 \text{ „} \\ \text{„} \quad &184° \text{ „ } 0\,00124 \text{ „} \\ \text{„} \quad &245° \text{ „ } 0\,00125 \text{ „} \\ \text{„} \quad &294° \text{ „ } 0·00128 \text{ „} \end{aligned}$$

These numbers indicate that the coefficient does not vary appreciably with temperature.

Volume of the Bulbs

Each bulb was heated for some hours in an air-bath to a temperature of approximately 550° C before being used.

Volume of Bulb 1.—1401 735   Mean of 10 determinations, varying from 1401 728 to 1401 743

Volume of Bulb 2 —Two rough determinations were made before use These gave

$$1385\,980 \quad \text{and} \quad 1385\,959$$

Immediately after the experiments on the S B P two very careful measurements were made (in July), viz —

$$1385\,9870 \quad \text{and} \quad 1385\,9886$$

Three months later, two more, carried out with equal care, gave

$$1385\,9835 \quad \text{and} \quad 1385\,9833$$

The difference between the two last sets is small, but represents, I think,

a real change in volume   In working out the results 1385·987 has been taken as the volume   If the true value be ¼ mgrm smaller, then the coefficient of expansion of the gas would have to be increased by 1₄ unit (with six significant figures), and the value of S B P by 001₅°   It may be mentioned that this bulb was heated on one occasion to 550° C for seven hours in free communication with the air, and on the following day for another six, it was then filled with mercury, and the freezing-point taken within an hour of being removed from the air-bath   It was kept in ice continually for 24 hours, no change of volume to a milligramme could be detected

Coefficient of Expansion of the Bulb

It was originally intended to determine the expansion of the bulb by the weight thermometer method   In view, however, of the results obtained,[*] this idea had to be abandoned   I have, therefore, made use of the following values derived from other observers :—

Between 0° and 100° C, mean coefficient of expansion, 145×10^{-8},
„   0° „   445° C   „   „   „ 168×10^{-8}

An increase of 10×10^{-8} in the first coefficient will increase the coefficient of expansion of the gas by 14 units with six significant figures, and diminish the S B P by 0 017°, while a similar increase in the second coefficient will increase the S B.P by 0 032°

The Barometers

For description of these reference can be made to the earlier paper   As the German glass used for the standard barometer was somewhat faulty, thus rendering the setting more difficult, it was replaced by English glass, which was found much more satisfactory   The length of the barometer was determined before and after the experiments on the boiling point of sulphur by comparison with an invar scale recently redetermined at the National Physical Laboratory   The values for the length of the barometer were as follows —

Length at 16°

| April, 1911   . | 75 9776 |
| October, 1913 | 75 9770 |

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* Eumorfopoulos, 'Phil. Mag,' [6], vol. 23, p. 653 (1912)

Course of the Experiments.

As before, only three temperatures were observed, viz., W F P, W.B P and S.B.P.

The ice was tested regularly every day with silver nitrate and with barium chloride solutions   The former very seldom gave even an opalescence with the melted ice, the latter did so as a rule, but not as much as was given by a solution of sulphuric acid with freezing point — 0 001° C. Only on one or two occasions was it necessary to reject the observations due to the precipitate exceeding this amount

The S B P apparatus is similar in construction to the one given in my former paper, except that it was of larger dimensions   The part of the boiler exposed to the flame is 7 cm, high, the portion covered by asbestos 32 cm , and the uncovered portion above this 5 cm   The diameter is 11 5 cm , while the walls are just a little over 1 mm thick. A thin tin-plate screen surrounded, but did not actually touch, the bulb so as to prevent radiation The shape of the screen is indicated in fig 3 by the dotted line   To allow circulation of the vapour four holes about 1 cm diameter were punched in the screen at X. There were also openings at Y In addition a horizontal plate was placed 2–3 cm above this screen , this plate almost closed the opening of the bath   A plate of uralite with the necessary openings for the four tubes was cut into two and placed over the mouth of the bath   Into a fifth opening, nearly 2 cm in diameter, was luted a glass tube, in which the line of condensation of the vapour could be observed This occurred a couple of centimetres above the uralite plate. To test how far the temperature depends on the size of the flame heating the bath, the gas was turned very low, so that the sulphur was just boiling   The temperature became apparently steady   The gas supply was now increased, and the temperature rose about 0 06°   A further increase indicated no rise of temperature (to 0 002°), by this time the vapour was alight, and large flames about 10 cm long were shooting out horizontally between the top of the bath and the uralite. It would thus appear that with this bath it is almost impossible to superheat the vapour

The Experiments.

The bulb was cleaned with nitric acid and with mixed chromic and sulphuric acids, it was then thoroughly washed with distilled water, dried, and connected up with the rest of the apparatus by means of the wax joints already mentioned   It was then heated for a few hours to 550° (approximately), evacuated with a Fleuss pump, and finally with charcoal in liquid air,

Connection was made to the pump through the mercury gauge (tube O, fig 2)
The method of connection is shown in fig 4

Air was passed into the thermometer after purifying it by means of potash, sulphuric acid and phosphoric anhydride. The bulb was several times evacuated, and finally filled with air in the cold at a pressure of 76 cm.   On determining several times the coefficient of expansion it was found to be

$$0\cdot0036756$$

This value is evidently too high, so the bulb was evacuated again in the cold and refilled, no other change being made   The coefficient was again found to be

$$0\ 0036756$$
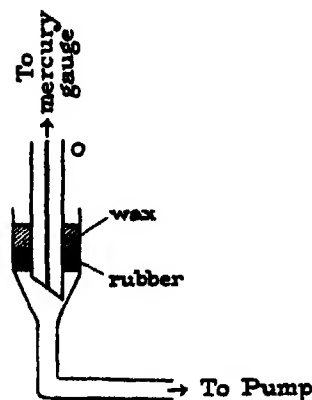
As the error could be accounted for, if the compensation tubes were not acting, the junction of the silica and the glass at the wax joint was examined, but was found to be in order   The volume of the bulb was roughly determined, but no appreciable change was found

As it was thought that some impurity might come from the sulphuric acid or the phosphoric anhydride, the former was done away with, while the latter was changed, Kahlbaum's being used this time   The coefficient found was

$$0\ 0036755$$

The cause of these high values has so far remained a mystery   If due to an impurity in the air, it seems extraordinary that the quantity should be so constant (no burners were alight in the room at the time of filling, no other experiments were going on, and the window was open), while, if the source of the trouble is something condensed on the silica, it seems equally remarkable that this impurity does not get permanently condensed on the glass bulbs kept at 0° C , on the contrary, the coefficient found on heating the silica from 0° to 100° agreed perfectly with that found on cooling down again

It was now decided to try some experiments with nitrogen   This gas was prepared in the usual way by heating together in solution potassium nitrite and ammonium chloride   The resulting gas was passed through a tube containing solid potash sticks, another containing phosphoric anhydride, then through a red hot tube containing copper and copper oxide, then again over potash and phosphoric anhydride, and finally through a glass spiral

To mercury gauge

O

wax

rubber

→ To Pump

Fig 4

immersed in liquid air   This last tube was connected to the one first mentioned, and by a suitable arrangement the gas could be circulated This was done continuously for some three or four hours   It should be mentioned that the whole system of tubes was evacuated before letting in the gas , then some gas was let in, and the tubes again evacuated before proceeding with the final preparation

After exhausting the bulb at a temperature of over 500°, with a charcoal vacuum, the nitrogen was introduced after passing it through a spiral immersed in liquid air   The pressure being 76 0, the coefficient was found to be

$$0\ 0036714$$

The bulb was again evacuated at 550°, left at this temperature for about two hours in connection with the charcoal tube, filled with nitrogen at the high temperature, and the gas drawn backwards and forwards for about half-an-hour through the spiral and over sodium-potassium alloy, the former tube being the nearer to the thermometer   At a pressure of 76 3 cm , the coefficient was now

$$0\ 0036702$$

As the diminution in the coefficient is quite large, the bulb was again heated up, but not evacuated, the gas being merely passed to and fro through the spiral and over the alloy   At a pressure of 78 4 cm   the coefficient was numerically the same , this means, in reality, a diminution of three in the last figure   As this was deemed satisfactory, the following measurements of the coefficient were made —

Up[*]	367074×10^{-8} ⎫	Down	367004×10^{-8}	
Down	367012 ⎬	Down	367034	
Up	367031 ⎫	Down	367016	
Down	367022 ⎬	Down	367015	

The mean of these, omitting the first value, is

$$367019 \times 10^{-8}$$

[*] The word " up" means a value obtained on heating up the bulb from 0° to the boiling-point , the word "down" on cooling down.   Numbers bracketed together are obtained for the *same* boiling-point

The following values for S B P were obtained, reduced to 76 cm by Harker's formula [viz, $0\,904\,(p-76)-\overset{\circ}{0}\cdot00519\,(p-76)^2$] —

Up	$444\overset{\circ}{}078\Big\}$ Mean	$444\overset{\circ}{\cdot}117$
Down	$444\,156$	
Up	$444\,170\Big\}$ „	$444\,170$
Down	$444\,169$	
Up	$444\,149\Big\}$ „	$444\,146$
Down	$444\,143$	
Up	$444\,144\Big\}$ „	$444\,138$
Down	$444\cdot131$	
Up	$444\,131$ „	$444\,131$
	Mean	$444\,140$

Unfortunately at this stage the oil-gauge tap got jammed, and in freeing it a little air went up the tubes As it was July, and I was leaving town, I merely pumped out the nitrogen and let in some dry air at 76 3 cm pressure and determined its coefficient , it was found to be

$$0\,0036710$$

The air remained in the bulb till October, when the latter was heated up to the usual temperature for some hours, pumped out with a Fleuss pump and with charcoal in liquid air, some nitrogen let in over sodium-potassium alloy and through the spiral in liquid air, pumped out again, and again filled with nitrogen, the gas being drawn to and fro over the alloy Finally the bulb was cooled to $0°$, the pressure adjusted, and the coefficient measured. It was found to be

$$0\,0036728$$

This coefficient is again too high, in spite of the fact that the heating up, etc , occupied two successive days, say 12 hours in all The above process was, therefore, repeated, i e , bulb was heated up, and the *same* nitrogen drawn to and fro through the usual tubes The coefficient at a pressure of 75 6 cm. was now found to be

$$0\,0036704$$

The same process was again repeated for two days, and at a pressure of 75 7 cm the coefficient was found to be

$$0\,0036701$$

As it was thought the gas was now sufficiently pure for measurements to be made, the following values for the coefficient were obtained .—

Up...	366999×10^{-8} ⎱	Up. .	366985×10^{-8} ⎱
Down .	366991 ⎰	Down.	366978 ⎰
Up .	366987	Up.	366994
Up	366981	Up	366990
Up	366979 ⎱	Up	366994 ⎱
Down	366990 ⎰	Down	366983 ⎰
Up	367008	Up	367004
Up	366997		

Mean $\qquad 366991 \times 10^{-8}$

And the following values for the S B P —

Up	$444°084$ ⎱ $444°106$	Up	$444°118$ ⎱ $444°120$
Down	444129 ⎰	Down	444122 ⎰
Up	444101 ⎱ 444092	Up	$444154 \quad 444154$
Down	444083 ⎰	Down	$444161 \quad 444161$
Up	444135 ⎱ 444134	Up	444151 ⎱ 444138
Down	444133 ⎰	Down	444124 ⎰
Up	444134 ⎱ 444128	Up	444127 ⎱ 444128
Down	444123 ⎰	Down	444129 ⎰
Up	444132 ⎱ 444120	Up	444089 ⎱ 444097
Down	444107 ⎰	Down	444105 ⎰

Mean $\qquad 444125°$

The occasional somewhat large differences between the " up " and " down " values made me suspect that the trouble of the high coefficient had not been entirely eliminated (it is obvious that this difference does not in any way depend on the observations at the S B P.), and I decided to repeat the whole set, substituting, however, a Toplei pump for the Fleuss When the nitrogen was prepared, it was noticed that a considerable amount of ammonia was given off, and, as it was feared that the purifying tubes might not be able to cope with this impurity, a fresh quantity of the gas was prepared, and passed first through a sulphuric acid bulb, and then through the same tubes as in the previous preparation Before the measurements with the new gas were carried out, I made, at Mr J Rose-Innes' suggestion, a few observations at a lower pressure, so as to obtain the thermodynamic correction These experiments cannot claim the same accuracy as the ones carried out at a higher pressure In the first place, the sensitiveness of the oil-gauge is proportional to the pressure, and then serious trouble arose over the solubility of air in the oil (Fleuss pump oil) used in the oil-gauge. Occasional minute air-bubbles made their appearance at the points marked

A and B (especially A) in the accompanying figure   At the low pressure, oil slowly leaked into the oil-gauge through the tap   As air could not do so directly, the only explanation seemed to be that it got carried in by the oil in solution, the change of solubility in the pressure accounting for the air-bubbles   In addition, it was very likely that diffusion might take place through the oil   In fact, it was noticed that, if two W.F.P.'s were taken in succession (say on Friday and on Monday), the oil-gauge did not give the same reading on the two days.   The C side had apparently increased in pressure, presumably because the C tube is nearer the bulb C of the tap, from which the leakage apparently came
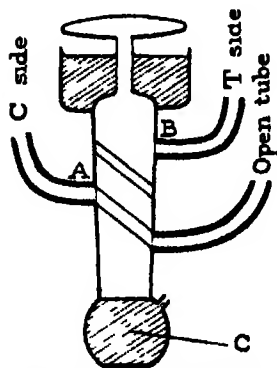
Fig 5 —Oil-gauge Tap

This change of pressure was measured on three separate occasions, and was found to be equivalent to a change of the W F P of 0 60 mgrm per hour—this is equivalent to a change in the coefficient of 0 80 per hour with six significant figures, and in the S B P of 00080° per hour   This correction has been applied in all the low pressure measurements , to show its importance, its magnitude is indicated in the tables of results

Owing to the pressure in the thermometer being smaller than the atmospheric, mercury could not be removed from the expansion bulb (bulb E) with the apparatus as it stood, nor could the oil-gauge be conveniently manipulated   To overcome these difficulties, a small piece of apparatus, shown in fig 6, was adapted to the thermometer   By adjusting the reservoir B, the pressure in A could be varied   Three tubes, with stopcocks, were sealed to A   One communicated with the atmosphere, the second was connected to the open tube of the oil-gauge (see fig 2), and the third to the bulb C, in which was collected the mercury from the expansion bulb

The experiments with the old gas at a pressure of 39 5 cm. gave the following results —

	Coefficient ×10⁸	Corrected for diffusion	
Up	366479 ⎤	(24 hours)	366498 ⎤
Down	366499 ⎦	(4 „)	366496 ⎦
Up	366485 ⎤	(68 „)	366539 ⎤
Down	366580 ⎦	(4 „)	366577 ⎦
Up	366302 ⎤	(188 „)	366452 ⎤
Down	366640 ⎦	(4 „)	366637 ⎦
Up	366555 ⎤	(20 „)	366571 ⎤
Down	366652 ⎦	(4 „)	366649 ⎦
Up	366601 ⎤	(20 „)	366617 ⎤
Down	366590 ⎦	(4 „)	366587 ⎦

Coefficient $\times 10^8$		Corrected for diffusion	
Up	366531 ⎫	(68 hours)	366585 ⎫
Down	366564 ⎭	(4 ,,)	366561 ⎭
Up	366504 ⎫	(20 ,,)	366520 ⎫
Down	366556 ⎭	(4 ,,)	366553 ⎭
Down	366575	(4 ,,)	366572
	Mean	366561×10^{-8}	

S B P		Corrected for diffusion	
Up	444·407° ⎫	(20 hours)	444·423° ⎫
Down	444·439 ⎭	(4 ,,)	444·436 ⎭
Up.	444·383 ⎫	(20 ,,)	444·399 ⎫
Down	444·414 ⎭	(4 ,,)	444·411 ⎭
Up	444·334 ⎫	(20 ,,)	444·350 ⎫
Down	444·339 ⎭	(4 ,,)	444·336 ⎭
	Mean	444·392°	
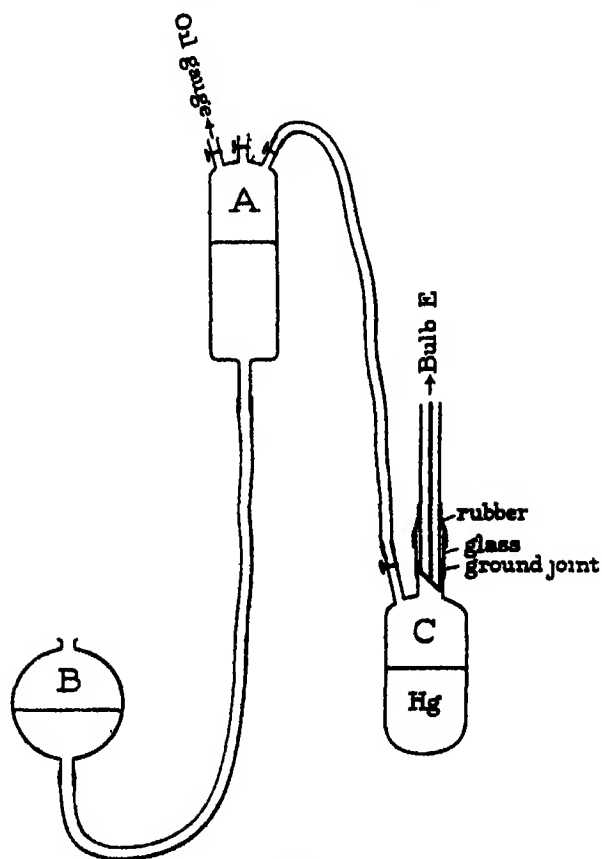
FIG 6.

Once, when the nitrogen was giving an abnormal coefficient, an attempt was made to see if any gas was given off by the bulb   For this purpose, an ordinary vacuum tube with electrodes was connected to the tube coming from the thermometer.   The bulb, kept in ice, was evacuated with the Topler until practically no discharge passed   On placing the bulb *rapidly* in boiling water, in general, no change of luminosity was observed, although the nitrogen was on one occasion left for a month in the bulb to enable the silica to absorb the gas, if it felt inclined to do so   Once only was there a sudden increase of luminosity

For the following experiments, the fresh sample of nitrogen was used, and the second bulb —

$$\text{Pressure} = 79\ 2\ \text{cm}$$

Coefficient—

Up	366987×10^{-8}	Down	367011×10^{-7}
Down	366997	Down	367003
Down	367013	Down	367004
Down	367005	Down	367009
	Mean	367005×10^{-8}	

In taking the mean, I have counted as one observation the first two values, so as not to give undue weight to a single boiling point observation

S B P —

Up	$444\overset{\circ}{\ }144$	Up	$444\overset{\circ}{\ }126$
Down	444 113	Down	444 112
Up	444 120	Up	444 118
Down	444 116	Down	444 121
Up	444·132	Up	444 143
Down	444·120	Down	444 140
	Mean . 444 125		

The pressure was now reduced to 41 5 cm   In all these observations, a S B P was taken in the morning, a W B P in the afternoon, and finally, about an hour later, a W F.P   The correction for diffusion is then practically negligible in the case of the coefficient, the values for the latter were as follows.—

366578×10^{-8}	366601×10^{-8}
366576	366593
366583	366598
366598	366581
366591	366573
Mean .. 366587×10^{-8}	

The following values for the S B P were obtained :—

Corrected for diffusion

Up	444 126 ⎤	(68 hours)	444 180 ⎤
Down	444 390 ⎦	(4 „)	444 387 ⎦
Up	444 326 ⎤	(20 „)	444 342 ⎤
Down	444 437 ⎦	(4 „)	444 434 ⎦
Up	444 281 ⎤	(44 „)	444 316 ⎤
Down	444 336 ⎦	(4 „)	444 333 ⎦
Up	444 319 ⎤	(20 „)	444 335 ⎤
Down	444 342 ⎦	(4 „)	444 339 ⎦
Up	444 268 ⎤	(92 „)	444 342 ⎤
Down	444 345 ⎦	(4 „)	444 342 ⎦
Up	444 332 ⎤	(20 „)	444 348 ⎤
Down	444 429 ⎦	(4 „)	444 426 ⎦
Up	444 368 ⎤	(72 „)	444 426 ⎤
Down	444 371 ⎦	(4 „)	444 368 ⎦
Up	444 330 ⎤	(20 „)	444 346 ⎤
Down	444 366 ⎦	(4 „)	444 363 ⎦
Up	444 332 ⎤	(44 „)	444 367 ⎤
Down	444 350 ⎦	(4 „)	444 347 ⎦
Up	. 444 286 ⎤	(20 „)	444 302 ⎤
Down	444 307 ⎦	(4 „)	444 304 ⎦
	Mean		444 356°

As a rule, in manipulating the oil-gauge, it was possible to prevent any of the small air-bubbles that formed at the tap from passing up into the thermometer   Occasionally (especially over the week end) this was not easy, and for the first S B P there is a note in my book that some minute bubbles passed up both sides.   I have, therefore, taken no account of it in obtaining the mean

After this, the nitrogen was removed, and the thermometer filled with air that was passed through potash solution, a phosphoric anhydride tube, and a spiral immersed in liquid air   The following observations were made —

Pressure = 81 1 cm

Coefficient—

Up .	.	367098×10^{-8} ⎤	Down	...	367083×10^{-8}
Down		367043	Up	.	367107 ⎤
Down		367069	Down	. .	367076 ⎦

Mean .... 367079×10^{-8}

S B P—

Up	444·173	Up	444·156
Down	444·105	Down	444·077

Up	444·136
Down	444·079

The variations are much larger than in the case of nitrogen at a corresponding pressure   Further, the " down " values of the S B P are in all three cases about 0·07° smaller than the " up " values   The difference is in the same direction in the two similar coefficient values   After the last W F P the bulb was heated up to 100° for 10 or 15 minutes, letting out mercury so as to keep the pressure constant, then it was cooled to 0° for a similar period, mercury being introduced   This was done three times in all in succession   The final result was, after all corrections are made, as if 22 mgm were driven out in the process   This would make a difference of 30 units (with six significant figures) in the coefficient, and is in the same direction as the above-noted differences

After this experience I thought it was useless to proceed further with air   I had intended carrying out some measurements with argon, but it seems preferable first to clear up the source of the air discrepancies, and a search must also be made for an oil which dissolves less gas than the Fleuss pump oil

The following coefficients have thus been found for nitrogen —

Pressure	Coefficient ×10⁶	Pressure	Coefficient ×10⁶
78·4	367019	39·5	366561
75·7	366991	41·5	366587
79·2	367005		

To compare these, we shall reduce the first three to a common pressure 79·2 and the last two to 41·5, with the following result —

Pressure	Coefficient ×10⁶	Pressure	Coefficient ×10⁶
	367028		366583
79·2	367030	41·5	366587
	367005		

I consider that the last value of each set is the more reliable.   If we adopt these, the value of the coefficient for a pressure of 0 cm. is

0·00366127,

the reciprocal of which is

273·129.

The values for S B.P are as follows :—

Pressure	Temperature	Pressure	Temperature
	°		°
78·4	444 140	39 5	444 392
75 7	444 125	41 5	444 356
79·2	444 125		

Reducing these, as in the case of the coefficient, we have —

Pressure	Temperature	Pressure	Temperature
	°		°
79 2	$\begin{cases} 444\ 135 \\ 444\ 104 \\ 444\ 125 \end{cases}$	41 5	$\begin{cases} 444\ 380 \\ 444\ 356 \end{cases}$

Adopting as before the last values, we get for the value of S B P on the thermodynamic scale

$$444\ 61°$$

Experiments that are now being carried out on the Joule-Thomson effect will, it is hoped, throw further light on these reductions to the thermodynamic scale

There is no need to collect here previous results on the S B.P , as this has been admirably done by Waidner and Burgess, and by Day and Sosman *

The principal results of this research are as follows —

1 The thermodynamic correction to the S B P has been obtained experimentally, and the value of the S B P on the centigrade thermodynamic scale found to be

$$444\ 61°$$

2. The value of the melting point of ice on the absolute centigrade thermodynamic scale is

$$273\ 13°$$

I wish to thank the Government Grant Committee of the Royal Society for a grant towards the expenses of this research

The Occurrence of Ozone in the Upper Atmosphere.

By J. N. Pring, D Sc., Lecturer on Electro-Chemistry in the University of Manchester

CONTENTS

Part 1 —*Introduction*

The question of the occurrence of ozone in the atmosphere has been for a long time a subject of much speculation, on account of the important bearing it has, both from physical and chemical considerations, in dealing with many atmospheric phenomena

Many workers have shown the marked absorption effects that small quantities of ozone have on ultra-violet light [*]   The view has also been put forward that this gas plays an important part in contributing to the blue colour of the sky [†]

The active chemical properties of ozone would, moreover, if present, be expected to play a very important part in determining the salubrity of the atmosphere, on account of its intense bactericidal action, and its general property of destroying organic matter

Although a very large amount of work has been done with a view to ascertain the presence and to determine the quantity of ozone in the atmosphere, very few satisfactory attempts have been made to distinguish between this gas and other substances, such as oxides of nitrogen and hydrogen peroxide, which have very similar chemical properties

The results obtained by different investigators are very discordant, and many of the methods used in extended measurements have since been found quite unreliable, and to give rise to misleading conclusions.

It appears now to be generally accepted that all the forms of test papers

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[*] *Cf* Krüger and Moeller, 'Phys Zeit,' vol. 13, p. 729 (1912), Fabry and Buisson, 'Compt. Rend,' vol 156, p 782 (1913)

[†] *Ut infra.*

and colorimetric methods which have been used so far are not applicable for quantitative results.   In some earlier work by the writer, in conjunction with W. Hayhurst,[*] a series of measurements on the quantity of ozone in the atmosphere were attempted.   By making use of kites and balloons, it was shown that definite small quantities of ozone occur at high altitudes, though no conclusive distinction between this gas, hydrogen peroxide, and oxides of nitrogen was made.

Thierry[†] had previously made measurements in the Alps at different altitudes.   The method used consisted in drawing measured volumes of air through a solution of potassium arsenite, which by reaction with ozone was oxidised to arsenate, and the remaining arsenite was estimated by titrating with a solution of iodine.   Some preliminary qualitative tests showed that there was no appreciable quantity of oxides of nitrogen or hydrogen peroxide present to complicate the reaction.   Definite quantities of ozone, which increased with the altitude, were found.

H. N. Holmes[‡] carried out a series of qualitative tests by exposing papers impregnated with starch and potassium iodide.   Definite indications of ozone were found, the amount being greater in winter than in summer.

Part 2.—*Some Distinctive Chemical Properties of Ozone.*

A large amount of preliminary work has been done to find some method of determining ozone chemically which would not be vitiated by other gases present in the atmosphere, and which would be simple in application.   It was necessary that the method should be capable of use in light apparatus which could be attached to small balloons.

The reagent which was considered most suitable in this application was an aqueous solution of pure potassium iodide.   It was found in these preliminary experiments that a concentrated solution reacts with ozone, even when this gas is present at high dilutions, with great rapidity.   This is also the case at temperatures as low as $-50°$, when the gas is passed over the surface of the solid reagent.   As the reaction which takes place between ozone and potassium iodide is known to be very complex, it was hoped that an examination of the products obtained would enable a distinction to be made between ozone and other possible reacting gases in the atmosphere.

Reaction between Potassium Iodide, Ozone, Oxides of Nitrogen, and Hydrogen Peroxide.—The measurements which were made to ascertain the reactions which take place between these gases and potassium iodide showed that, in

* 'Chem. Soc. Trans.,' vol. 97, p. 868 (1910).
† 'Compt. Rend.,' vol. 124, p. 460 (1897).
‡ 'Amer. Chem. Journ.,' vol. 47, p. 497 (1912).

the case of ozone, in accordance with an effect of mass action, the nature of
the products given by this reaction depends on the total quantity of this gas
which has been passed, and also varies in a high degree with the concentra-
tion of ozone per unit volume of gas, even when the same total amount of
ozone has been passed *

It was found that, at a dilution of 1 part in 100,000, the reaction with
potassium iodide yields hypo-iodite and free iodine, but no iodate

The products can be simply estimated by titration with standardised
sodium thiosulphate solution, and the absence of iodate ascertained by then
acidifying the solution. Any iodate present would cause an immediate
liberation of iodine

Measurements made on the influence of temperature showed that, below
$-24°$, when the reagent was solid, the above relation no longer applied, as, in
this case, iodate was formed by ozone at all concentrations

Oxides of nitrogen were found to react with potassium iodide to give
mainly iodate at all concentrations. In this way a basis is provided for the
distinction of ozone from nitrogen peroxide when the gases are present at
high dilutions, and if the temperature is not below $-24°$

Hydrogen peroxide at high dilutions when reacting with potassium iodide
gave products similar to those obtained with ozone, so that this reagent does
not furnish a distinction between these two gases. However, the difficulty
can be overcome by means of a separate test, using titanium sulphate
dissolved in sulphuric acid, which gives a yellow coloration in presence of
very small quantities of hydrogen peroxide, while ozone produces no effect

It is seen below that, by the application of these tests to atmospheric
measurements at high altitudes, it was established that there was no
detectable quantity of hydrogen peroxide or oxides of nitrogen present, but
in all cases definite quantities of ozone were found.

Part 3 —*The Action of Ultra-violet Light on Air.*

The formation of ozone by the action of ultra-violet light on oxygen has
been demonstrated by a number of investigators and it has also been shown
that this reaction takes place when air is used in place of oxygen.

It has been observed, on the other hand, that ozone is decomposed by ultra-
violet light.

Regener† found that an equilibrium stage is obtained when with a certain
concentration of ozone no further change is produced on exposing to the light

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* For further discussion of these reactions, see Pring, 'Chem. News,' vol. 109, p. 73
1914).

† Regener, 'Ann d Phys,' vol. 20, p. 1033 (1906)

It was found that this equilibrium varies with the temperature and with the nature of the light. Measurements showed that only light of wave-length below 200 $\mu\mu$ is effective in causing the production of ozone from oxygen. This corresponds with the observation of Kreusler that the absorption point of light by oxygen occurs at 193 $\mu\mu$ and below.

It was also found by Regener that the rays which are effective in causing the decomposition of ozone lie between 185 and 300 $\mu\mu$, which agrees with the measurement made by Meyer, according to which ozone absorbs light of wave-lengths up to 257 $\mu\mu$. Meyer draws attention to the fact that the solar spectrum ceases at about 293 $\mu\mu$, and attributes this to the absorption by ozone in the atmosphere.

Von Bahr found that the rate of decomposition of ozone on standing increases rapidly as the pressure is lowered, and thus considers it improbable that any considerable quantity of this gas can exist in the upper atmosphere.

As is recalled below, very little experimental work has been conducted to ascertain the possibility of producing oxides of nitrogen and hydrogen peroxide by ultra-violet radiation.

An investigation was made in this work on the action of ultra-violet light on air, under different conditions of pressure, humidity, etc., in order to obtain some idea of the concentration of ozone that can be reached in this way under the different conditions, and also to see if any other products, such as oxides of nitrogen and hydrogen peroxide, are produced by this action. The apparatus designed for the exposure of the air is shown in fig. 1, and at A, fig. 2.

The main feature in the source of ultra-violet light used consisted in the application of the light, derived from a mercury arc, after passing through a quartz partition, directly to the air undergoing reaction. In this way absorption of the rays by any intervening layer of air was avoided. The quartz tube containing the mercury arc, B, was surrounded with a quartz bulb fitted with the inlet and outlet tubes e, e, through which the air was circulated. The outside walls of the annular vessel were cooled by submerging the whole apparatus in a vessel of water. The arc was started by means of an induction coil in the following manner. A potential difference of 100 to 200 volts was connected to the terminals T_1, T_2, after first passing through the lamp resistances joined in series at R (fig. 2). The secondary circuit of the coil made connection with one of these terminals at T_1 and with a wire W, wrapped round the centre of the annular jacket of the lamp. On working the induction coil by means of a tapping key K, a glow discharge was made to pass through the lamp, which started an arc between the reservoirs of mercury at the terminals. When the lamp was immersed in a bath of water, this method of starting was still more
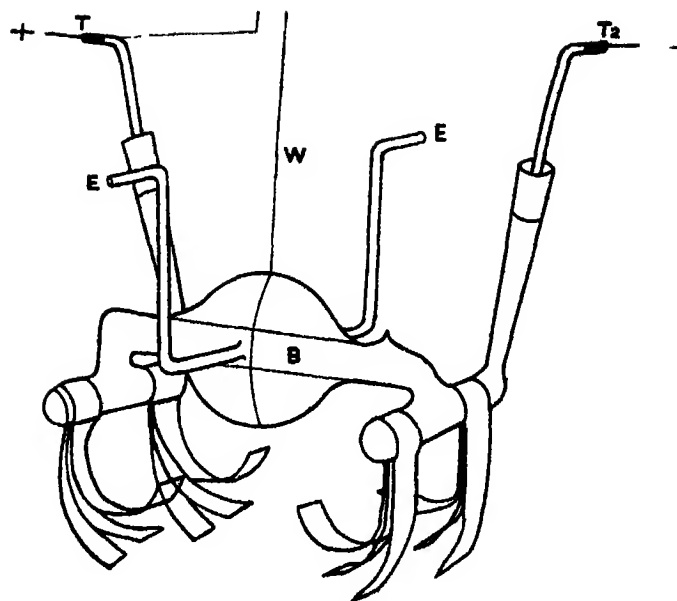
FIG 1.
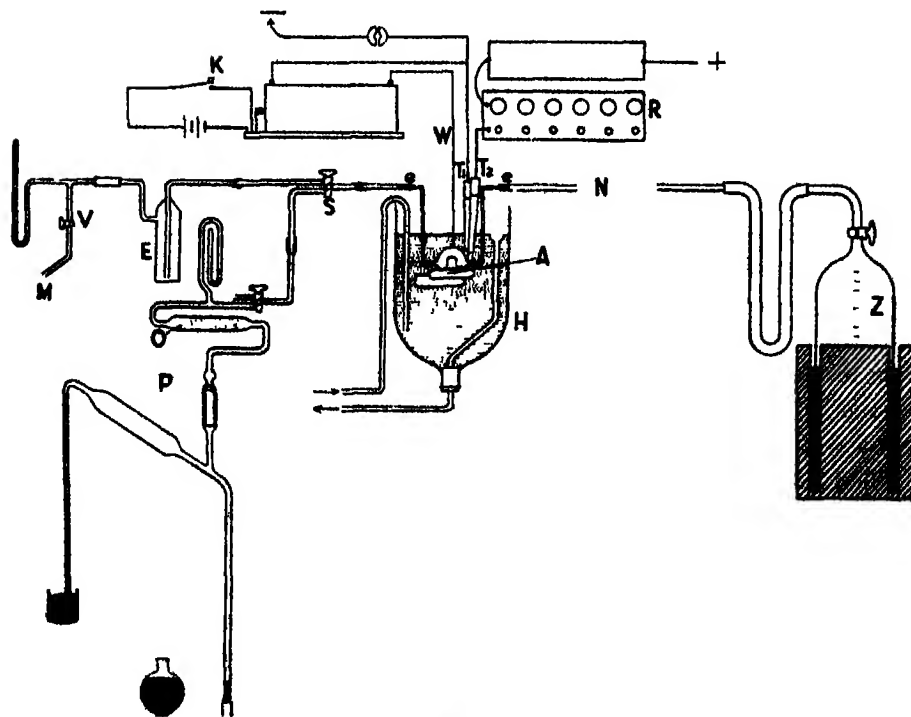
FIG 2

effective than when in air, though with the water cooling a higher voltage (200) was necessary to ensure continuous working.

A Topler pump (P) was connected with the apparatus by means of the two-way tap (S) for the purpose of exhausting and drying. The tube M could be connected with a water pump to aspirate gases at low pressures The reagent was placed in the wash-bottle E When estimating ozone, the solution used consisted of equal weights of potassium iodide and water. The water cooling of this apparatus did not of course suffice to maintain a uniform temperature of the contained air

In addition to this factor of temperature, other conditions prevailing in the upper atmosphere could not be reproduced in these experiments The nature of the ultra-violet light obtained from the mercury arc was of course limited by the transparency of the quartz, and would thus be expected to differ from the case of solar radiation acting on the uppermost layers of the atmosphere However, it was possible to obtain conclusive results on the relative formation of ozone, nitrogen peroxide, and hydrogen peroxide, with the particular light used.

Equilibrium Value of Ozone—In measuring the equilibrium value of ozone produced by circulating the air at very low speeds, it was found that the temperature of the lamp quickly imposed a limit to the concentration of ozone The highest yield of this gas was obtained when the arc was formed intermittently for a very short interval every half minute, thus minimising the rise of temperature A confined volume of air in the annular space of the lamp was exposed to the radiation. The arc was formed for 1 second every 30 seconds, and the ozone estimated after different intervals in a series of experiments. It was found that the quantity of this gas formed increased rapidly at first and afterwards slowly until, after 40 seconds total exposure, a maximum was practically reached containing 0·15 per cent. ozone.

A similar result was obtained when the experiment was conducted with pure dry oxygen, in this case the maximum amount of ozone formed was 0·2 per cent.

E. Regener (*loc. cit*), when investigating the equilibrium in the production of ozone from oxygen at different temperatures, found this to be 3·4 per cent. at 20°, and 2·7 per cent. at 54° The discrepancy is probably due to differences in the types of apparatus used, as the equilibrium value would be determined by the relative transparency of the quartz for light of different wave-lengths.

Influence of Water Vapour on the Formation of Ozone.—It was found that a more favourable yield in the formation of ozone by ultra-violet

light is obtained with dry air or oxygen than in the case of the moist gas.[*]

The smaller yield of ozone in the case of moist air is probably due to the formation of traces of hydrogen peroxide, which reacts with ozone according to the equation

$$H_2O_2 + O_3 = H_2O + 2O_2$$

Effect of Pressure on the Formation of Ozone —The apparatus used for this measurement was arranged as shown in fig 2 The reaction vessel and connecting tubes were exhausted by means of the Topler pump P, containing phosphorus pentoxide at O.

The air was stored in the gas-holder Z, where it could be dried by leaving in contact with phosphorus pentoxide for several days By means of the tap S, which was lubricated with phosphoric acid, the gas, after passing through the radiation vessel, could be led through the reagent placed in the wash-bottle E In the comparative experiments 200 c c of air was passed in equal intervals of time, but at pressures varying from 760 to 30 mm

It was found that a marked fall in the ozone formation occurred with reduction of pressure. Thus, at 760 mm, the concentration reached was 0·01 per cent, and at 30 mm 0 0014 per cent

Formation of Hydrogen Peroxide—The action of ultra-violet radiation on water has been investigated by Kernbaum,[†] who found that a slight decomposition slowly takes place according to the equation

$$2H_2O = H_2O_2 + H_2$$
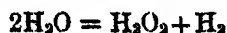
Chlopin[‡] investigated the formation of hydrogen peroxide from moist air when submitted to the radiation from a mercury arc lamp constructed of quartz The air was circulated through the reaction vessel at a speed of 35 litres per hour, and then passed through a solution of titanic acid dissolved in dilute sulphuric acid. After passing the gas for 10 minutes this reagent assumed a slight yellow colour, indicating the presence of traces of hydrogen peroxide

In the present work experiments were made to detect the formation of hydrogen peroxide by passing 60 litres of moist air through the apparatus during two hours, and leading through a solution of titanic acid in sulphuric acid and contained in a small glass spiral washer. No change in colour was observed A comparative test made by taking hydrogen

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[*] *Cf* Warburg and Leithauser, 'Ann. d. Phys,' vol. 20, p. 751 (1906).

[†] 'Le Radium,' vol 6, p. 225 (1909).

[‡] 'Zeit anorg. Chem.,' vol. 71, p. 198 (1911).

peroxide solution showed that it is possible to detect with certainty the presence of 0.1×10^{-6} grm equivalent of this compound with the above reagent In 60 litres of air this would correspond to a volume of 1.8×10^{-6} per cent. The amount formed under the conditions of the above experiment must therefore be below this value, which is very small compared with the ozone

As hydrogen peroxide is decomposed by ozone, it is doubtful whether any appreciable quantity would be permanently stable in presence of the latter gas

Formation of Oxides of Nitrogen—It has not yet been established whether oxides of nitrogen are formed by ultra-violet light, though Chlopin (*loc cit.*) obtained evidence of the formation of traces of this gas by applying metaphenylenediamine as a colorimetric test This method is extremely sensitive and open to doubt when applied in this connection In the present work, use was made of a method devised by Fischer and Marx[*] for distinguishing nitrogen peroxide from ozone, which depends on the fact that, when a mixture of the gases is passed into liquid air, the former separates as a white solid while the latter dissolves. Measurements were made in the present case with purified air which was circulated through the radiation apparatus during intervals of several hours, and then passed into liquid air After filtering off the solid particles, these were allowed to evaporate and pass into a gas-holder. No nitrogen peroxide could be detected in this gas by applying potassium iodide or tetramethyl base paper These results show that, as in the case of hydrogen peroxide, if any nitrogen peroxide is produced by ultra-violet light, as used in these experiments, the quantity is negligibly small when compared with the ozone

Part 4.—*Atmospheric Measurements at High Altitudes.*

A. *In the Alps, at Altitudes between* 2000 *and* 3500 *metres*—The absorbing vessel which was used to contain the reagent was the same as that employed in the earlier work of Hayhurst and Pring (*loc cit.*), and consisted of a spherical glass bulb of 5 cm diameter (B, fig 3), which was provided with an inlet and outlet tube 1 cm internal diameter terminating in conical funnels (C, C) on the outside, and projecting, on the inside, for some distance inside the bulb In this way a quantity of reagent could be placed inside the bulb and secured against loss when the apparatus was placed in any position. A free circulation of air through the vessel took place, when this was placed horizontally and exposed to a wind. The glass

[*] ' Ber.,' vol. 39, p. 2557 (1906).

funnels C, C, were extended by means of paper (D, D), and the whole enclosed in a cage of hard spring wire (BB) for protection. The glass vessel was blackened on the outside and also covered with black cloth to protect the reagent from light.
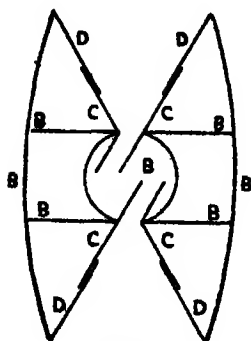
By placing a fuming liquid in the vessel and exposing to a wind, the air in passing through was seen to assume a rapid circulatory motion inside The efficiency of the absorption of ozone during this passage was tested by taking a vessel of similar construction, placing the potassium iodide reagent inside, and then joining the vessel in series with a wash-bottle containing the same reagent. On passing ozonised air through the two vessels in succession, and varying the speed of circulation, it was found that even at higher velocities than those subsequently given by the atmosphere, more than four-fifths of the ozone was in every case absorbed by the first vessel.

Fig 3

Volume of Air Circulated through the Reaction Vessel during a Measurement.—An approximate calibration of the volume of air circulated, which was assumed to be directly proportional to the velocity of the wind, was made by placing some pure benzene in the vessel, and after exposing for definite intervals to a wind of known velocity, noticing the loss in weight

The vessel was first calibrated in terms of the readings given by a portable anemometer kindly lent by the Meteorological Office, and then by comparison with a standardised anemometer at the Manchester University Observatory, the readings were reduced to miles per hour.

Results of Calibration

	Temperature of benzene	Units, anemometer scale	Loss of weight of benzene	Loss of weight per unit of anemometer scale
			grm.	grm.
Vessel 1	18·0°	135	5 30	0 0392
,, 1	18·0	95	4·70	0 0495
,, 1	16 5	70	2·67	0 0382
,, 2	17 0	81	3·55	0 0440
,, 2	17·0	97	4 35	0 0449
Mean	17 0	—	—	0 0433

Since the vapour pressure of benzene at 17° is 66·5 mm. and its molecular weight 78, it follows that 1 grm. of the saturated vapour will occupy

3·29 litres. The quantity displaced during a reading of 1 unit on the anemometer, viz, 0·043 grm., will therefore correspond to 0·141 litre.

The calibration of the anemometer showed that 1 unit corresponded to a horizontal flow of air of 0·027 mile, so that a flow of wind corresponding to a displacement past the apparatus of 1 mile corresponds to a circulation of 5·12 litres in the vessel.

Results of Measurements made in the Alps.—The tests, which lasted several days, were made near Scheidegg at an altitude of 2130 metres and at a point near the Jungfraujoch of 3580 metres altitude

Hydrogen Peroxide.—This was tested for by exposing titanic acid in presence of sulphuric acid to the wind in an apparatus similar to that used for the ozone estimation The colour of this reagent remained quite unchanged after exposing for two days at the different altitudes and under different conditions of weather, thus showing that there is no appreciable quantity of hydrogen peroxide in the atmosphere It was noticed, however, that freshly fallen snow or hail gave a very marked coloration with the reagent No tests were made with glacier water, though this would be expected to retain the hydrogen peroxide associated with the snow.

Nitrogen Peroxide.—In the experiments tabulated below, where estimations have been made of ozone, it was found that in no case was any potassium iodate formed on exposing the iodide in the reaction vessel to the atmosphere

Time of measurement	Altitude	Units, anemometer	Litres of air circulated	Total volume of ozone (at N T P)	Volume of ozone per unit volume of air
	metres			c c	
Aug 22-23, 1913—					
7 0 P M to 8 0 A M	2130	110	15 2	0 05	0 ·000008
Aug. 23—					
8.0 A M. to 7 0 P M	2130	813	113	0 31	0 ·0000027
Aug 23-24—					
7 0 P M to 8 0 A.M	2130	3176	438	0 ·87	0 ·00000197
Mean value at 6970 feet (2130 metres)					2 ·5 × 10⁻⁶
Aug 24—					
6.0 to 7.30 P M .. .	3580	1195	165	0 62	0 ·0000038
Aug. 25—					
8.50 A M to 5 45 P M ..	3580	10694	1470	7 ·1	0 ·0000048
Aug 26 —					
6.0 A.M. to 6 0 P.M.	3580	1520	210	1 ·18	0 ·0000056
Mean value at 11690 feet (3580 metres)					4 7 × 10⁻⁶

As pointed out above this shows the absence of any appreciable quantity of oxides of nitrogen.

Ozone Estimations.—These were made by placing about 7 c.c. of a mixture of equal weights of potassium iodide and water in the reaction vessel and placing on the ground horizontally in the direction of the wind The anemometer was erected in the neighbourhood

The mean quantity of ozone, viz., 2.5×10^{-6} at 2130 metres and 4.7×10^{-6} at 3580 metres, are in close agreement with the results obtained by de Thierry (*loc cit*), which gave 1.6×10^{-6} at 1050 metres and 4.4×10^{-6} at 3020 metres.

B. *Measurements made with Free Balloons*—For these measurements use was made of the hydrogen balloons which are used in meteorological investigations at the Manchester University These balloons with the attached instruments rise to an average height of about 10 miles and then burst. The deflated skin retards the rate of fall of the instruments to the ground A knowledge of the height attained and the temperature is obtained by a recording baro- and thermograph.

The reaction vessel for the ozone tests was of the same form as that used in the tests at ground level, and was suspended vertically from the balloon together with the other instruments.

A rough calculation of the amount of air which would pass through the vessel during an ascent and descent was made from the following data.—

From the calibration made above it was seen that the exposure of the vessel to a flow of wind corresponding to a displacement of air of 1 mile caused the passage of 5.12 litres Since 1 mile $= 1.6 \times 10^5$ cm, it follows that a displacement of 1 cm at atmospheric pressure will cause the circulation of $(5.12 \times 10^3)/(1.6 \times 10^5) = 0.032$ c c

On the assumption that the volume circulated is proportional to the displacement through the air, it follows that during an ascent and descent the mass of air passed through in grammes is given by $2(p_1 - p_2) \times 13.6 \times 0.032$, or $0.87 (p_1 - p_2)$, where p_1 is the atmospheric pressure in centimetres of mercury at ground level, p_2 that at the highest level reached, and 13.6 the density of mercury The volume circulated in litres (measured at N T P.) is therefore $0.675 (p_1 - p_2)$.

The values for the pressure at different altitudes have been taken from meteorological tables, as reproduced on p 215

At a height of about 6000 metres the temperature is always below the freezing point of the reagent ($-24°$) so that reaction must take place with the solid. It was seen in Part 1 that under these conditions the method applied did not enable a distinction between ozone and oxides of

nitrogen. However, in all measurements made up to 6500 metres, the latter gas was found not to be present in any appreciable quantity

Altitude	Pressure	Altitude	Pressure	Altitude	Pressure.
metres	mm	metres	mm	metres	mm
1000	673	4000	458	8000	267
1500	631	5000	401	9000	233
2000	586	6000	353	11000	168
3000	522	7000	308	20000	89

The reagent placed in the vessel consisted of 5 to 7 c.c. of the 50-per-cent potassium iodide solution as used in all the other measurements After being returned by the finder through the post the amount of solution remaining usually amounted to about 2 c c   The values given in the tables are calculated on the original quantity of reagent

Time of ascent	Mean direction of wind	Height attained	Estimated volume of air circulated	Weight of iodine liberated in total reagent		Potassium hydrate formed	Mean concentration of ozone in 1 volume air
				Free I_2 (+ hypoiodite)	Combined I_2 (as iodate, etc)		
Aug 3, 1909—		kilom	litres	mgrm	mgrm	mgrm	
9 0 P M	W S W	16 0	46 6	0 12	0 13		$4 8 \times 10^{-7}$
March 18, 1910—							
12 0 NIGHT	N	13 5	43 8	0 21	0 13	0 ·004	$6 8 \times 10^{-7}$
9 P M	N	8 5	34 7	1 02	0 70	Nil	$4 4 \times 10^{-6}$
March 19—							
2 0 A M	N	19 5	48 1	0 40	1 12		$2 8 \times 10^{-6}$
May 18—							
9 40 P M	S	17 0	47 5	0 76	0 76		$2 ·3 \times 10^{-6}$
May 19—							
2 10 A M	S	12 ·0	43 ·8	0 18	0 34	trace	$9 5 \times 10^{-7}$
6.30 A M	S	20 0	46 3	0 21	0 40		$1 1 \times 10^{-6}$
March 1, 1911—							
5.30 P M	N W	19 ·0	48 2	0 303	0 682	Nil	$1 8 \times 10^{-6}$
May 4—							
7 15 P M	N W.	20 0	46 3	0 612	2 36	Nil	$5 4 \times 10^{-5}$
Aug 6, 1913—							
8 0 P M	N N E	6 ·5	29 8	0 416	Nil		$1 ·2 \times 10^{-6}$
					Mean .		$2 1 \times 10^{-6}$

It is seen that, except in one case, a large part of the reaction had resulted in the formation of iodate. The one case in which this compound had not formed was where the ascent had only reached an altitude of 6 5 kilometres, where the temperature indicated was −31·5°   Since the cryoscopic point of the reagent is −24°, complete solidification had probably not occurred.

The fact that, as in the case of all measurements at lower altitudes, there was no iodate formed in this experiment, indicated the absence of oxides of nitrogen, and the formation of iodate in experiments at greater altitudes is presumably due to the reaction of ozone on the solid reagent, as was established in laboratory experiments.

By considering these results together with those made on ground level at altitudes up to 3 5 kilometres, the conclusion may be drawn that there is no detectable amount of hydrogen peroxide or oxides of nitrogen in the higher atmosphere, but that there is a definite small quantity of ozone   The amount of this last gas increases with the altitude up to 3 5 kilometres

The mean values estimated in the measurements made in the Alps were $2 5 \times 10^{-6}$ in one part of air at 2 5 kilometres altitude, and $4 \cdot 7 \times 10^{-6}$ parts at $3 \cdot 5$ kilometres.

In the measurements made with the balloons in this country, the mean volume of ozone between ground level and altitudes up to 20 kilometres gave an average value of $2 \cdot 1 \times 10^{-6}$ Even after allowing for the absence of this gas at lower levels on account of organic impurities, this value would indicate that there is no very great increase in the amount of ozone in the atmosphere between altitudes of 4 and 20 kilometres   The amounts measured, however, are known to be sufficient to exhibit marked absorption and chemical effects, and thus play an important part in the permeability to radiation and in the chemical purification of the atmosphere

Part 5 —The Part played by Ozone in Determining the Blue Colour of the Sky

The blue colour of the sky has been ascribed to a number of operating causes.   Firstly, the turbidity of the air or presence of small particles of dust has been shown to exert a selective reflection on light of different wavelengths

Secondly, it has been pointed out that the molecules of the air are themselves able to scatter radiation in a similar manner to the action of small particles of dust.*

Thirdly, the presence of ozone has been put forward by a number of investigators to account for this colour.†

The coloration has also been attributed to fluorescence phenomena produced by this gas ‡

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* Cf. Rayleigh, 'Phil. Mag ,' vol 47, p. 375 (1899) ; Schuster, 'Theory of Optics,' p. 328 (1909) ; 'Nature,' vol. 81, p 97 (1909) , King, 'Phil. Trans.,' A, vol. 212, p. 375 (1913).

† Cf Chappuis, 'Comptes Rendus,' vol. 91, p. 985 (1880), Hartley, 'Chem. Soc. Trans.,' vol 39, p. 111 (1881) ; Spring, 'Bull de l'Acad. Belge' (3), vol 36, p. 504.

‡ Cf Lallemand, 'Comptes Rendus,' vol. 75, p 707 (1872) ; Hartley, 'Nature,' vol. 39, p. 474 (1889).

It has been found* from spectrophotometric measurements on skylight that the distribution of intensity observed could not be altogether accounted for by the assumption of an atmosphere conforming to Rayleigh's formula nor of a turbid medium containing coarser particles These, and the results of other investigators, indicate that there is a blue absorption colour of the air.

In the present work the results of the approximate measurements made on the quantity of ozone in the atmosphere at altitudes ranging up to 20 kilometres supply data which enabled a rough comparison to be made in the laboratory of the depth of colour given by ozone of equivalent amount

For this experiment a glass tube of 2 8 metres length and 4 cm diameter was taken   The walls were provided with side tubes, one near each end, to enable the passage of the ozonised gas through the tube   The two ends of the main tube were covered by thin plates of glass, which were cemented by sodium silicate solution so as to make air-tight connection.

The outside of the tube was wrapped with black paper, and a white paper disc placed over one of the end plates   On illuminating this by daylight and sighting through the other end, the intensity of coloration produced on admitting ozone of known concentration could be observed.

The ozone for this purpose was prepared from oxygen by passing through a number of annular glass tubes where it was exposed to the silent electric discharge produced by an induction coil   After time had been allowed for the composition of the gas in the sighting tube to become uniform, an analysis of the gas was made by connecting the outlet side tube to a vessel containing acidified potassium iodide solution, and allowing a known volume of the gas to pass.

It is seen from the atmospheric measurements that, in this country, an approximate concentration of two parts of ozone in one million of air was found as the average amount of this gas between ground level and an altitude of 20 kilometres, while the amount found in the Alps at an altitude of $3\frac{1}{4}$ kilometres was five parts in one million. Taking this second value, and allowing 8360 metres as the height which would be occupied by the atmosphere if at N T P., this concentration of ozone in a vertical section of the atmosphere is equivalent to a layer of the pure gas of a thickness of 4·2 cm. (at N.T.P.).

The results given in the tables below record the observations made with the sighting tube when filled with oxygen containing different concentrations of ozone. The thickness of the layer of pure gas which is equivalent to this concentration is also given.

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* Nichols, 'Phys. Review,' vol. 26, p. 497 (1908).

Percentage concentration of ozone in oxygen	Equivalent thickness of layer of pure ozone	Colour observed
	cm	
0 20	0 55	Colour uncertain
0 86	1 0	Faint bluish green
1 7	4 7	Marked blue colour
2 8	7 8	Deep steel blue colour

It is difficult to compare the colour of the gas in a tube of this nature with that of the sky on account of a large influence exerted by the nature of the illumination

The results obtained, however, indicate that the presence of ozone is a contributing factor to the blue colour

This work is being extended with a view to determining more precisely the quantity of ozone in the upper atmosphere, its variation from time to time and with altitude, and its influence on the constant of solar radiation

Summary.

A method has been devised which enables an estimation to be made of ozone when at very high dilutions, and at temperatures down to $-60°$. With very dilute gases, the reagent used, consisting of an aqueous solution of potassium iodide, enables a distinction to be made between ozone and oxides of nitrogen, if the temperature is not below the freezing point of the reagent ($-24°$).

By applying a source of light given by a mercury arc in a quartz vessel it was found that ozone is formed up to a certain equilibrium stage   The rate of formation of the gas is only slightly lowered by the presence of water vapour, but decreases rapidly with falling pressure.

By exposing air to the source of light used, no formation of oxides of nitrogen or hydrogen peroxide could be detected   Estimations made of the quantity of ozone in the atmosphere at high altitudes in this country showed an average amount of $2\cdot5 \times 10^{-6}$ in one volume of air, and that no very large increase occurs between 5 kilometres and the highest altitude reached, viz. 20 kilometres   In the Alps, a mean value of $2\cdot5 \times 10^{-6}$ was measured at an altitude of 2100 metres, and $4\,7 \times 10^{-6}$ at 3580 metres.   No detectable amounts of oxides of nitrogen or hydrogen peroxide were found in either of the last two cases   It was found by colorimetric measurements in the laboratory that this last amount of ozone gives a marked blue colour, thus showing that ozone must be regarded as a contributing factor in determining the blue colour of the sky

In conclusion I wish to express my thanks to Sir Ernest Rutherford for the kind interest he has taken in this work, to Miss M White for the loan of meteorological balloons, and to the Director of the Jungfrau Railway for travelling facilities he generously extended

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On the Diffraction of Light by Spheres of Small Relative Index.

By LORD RAYLEIGH, O M , F R S

In a short paper " On the Diffraction of Light by Particles Comparable with the Wave-length,"[*] Keen and Porter describe curious observations upon the intensity and colour of the light transmitted through small particles of precipitated sulphur, while still in a state of suspension, when the size of the particles is comparable with, or decidedly larger than, the wave-length of the light   The particles principally concerned in their experiments appear to have decidedly exceeded those dealt with in a recent paper,[†] where the calculations were pushed only to the point where the circumference of the sphere is $2\,25\,\lambda$.   The authors cited give as the size of the particles, when the intensity of the light passing through was a minimum, 6 to $10\,\mu$, that is over 10 wave-lengths of yellow light, and they point out the desirability of extending the theory to larger spheres.

The calculations referred to related to the particular case where the (relative) refractive index of the spherical obstacles is $1\,5$.   This value was chosen in order to bring out the peculiar polarisation phenomena observed in the diffracted light at angles in the neighbourhood of 90°, and as not inappropriate to experiments upon particles of high index suspended in water. I remarked that the extension of the calculations to greater particles would be of interest, but that the arithmetical work would rapidly become heavy

There is, however, another particular case of a more tractable character, viz., when the relative refractive index is *small* , and although it may not be

the one we should prefer, its discussion is of interest and would be expected to throw some light upon the general course of the phenomenon. It has already been treated up to a certain point, both in the paper cited and the earlier one[*] in which experiments upon precipitated sulphur were first described. It is now proposed to develop the matter further

The specific inductive capacity of the general medium being unity, that of the sphere of radius R is supposed to be K, where K−1 is very small. Denoting electric displacements by f, g, h, the primary wave is taken to be

$$h_0 = e^{int}e^{ikx}, \qquad (1)$$

so that the direction of propagation is along x (negatively), and that of vibration parallel to z The electric displacements (f_1, g_1, h_1) in the scattered wave, so far as they depend upon the first power of (K−1), have at a great distance the values

$$f_1, g_1, h_1 = \frac{k^2 P}{4\pi r}\left(\frac{\alpha\gamma}{r^2}, \frac{\beta\gamma}{r^2}, -\frac{\alpha^2+\beta^2}{r^2}\right), \qquad (2)$$

in which

$$P = -(K-1)\ e^{int}\iiint e^{ik(x-r)}\,dx\,dy\,dz \qquad (3)$$

In these equations r denotes the distance between the point (α, β, γ) where the disturbance is required to be estimated, and the element of volume ($dx\,dy\,dz$) of the obstacle   The centre of the sphere R will be taken as the origin of co-ordinates.   It is evident that, so far as the secondary ray is concerned, P depends only upon the angle (χ) which this ray makes with the primary ray   We will suppose that $\chi = 0$ in the direction backwards along the primary ray, and that $\chi = \pi$ along the primary ray continued.   The integral in (3) may then be found in the form

$$\frac{2\pi R^2 e^{-ikr}}{k\cos\frac{1}{2}\chi}\int_0^{\frac{1}{2}\pi} J_1(2kR\cos\tfrac{1}{2}\chi\ \cos\phi)\cos^2\phi\,d\phi, \qquad (4)$$

r now denoting the distance of the point of observation from the centre of the sphere.   Expanding the Bessel's function, we get

$$P = -\frac{4\pi R^3(K-1)e^{i(nt-kr)}}{3}\left\{1-\frac{m^2}{2.5}+\frac{m^4}{2\ 4\ 5\ 7}-\frac{m^6}{2.4\ 6\ 5\ 7\ 9}\right.$$
$$\left.+\frac{m^8}{2\ 4\ 6\ 8\ 5\ 7\ 9\ 11}-\ \right\}, \qquad (5)$$

in which m is written for $2kR\cos\frac{1}{2}\chi$. It is to be observed that in this solution there is no limitation upon the value of R if (K−1)² is neglected absolutely.   In practice it will suffice that (K−1)R/λ be small, λ (equal to $2\pi/k$) being the wave-length.

* 'Phil. Mag,' vol 12, p. 81 (1881) ; ' Scientific Papers,' vol. 1, p. 518.

These are the formulæ previously given   I had not then noticed that the integral in (4) can be expressed in terms of circular functions   By a general theorem due to Hobson[*]

$$\int_0^{\frac{1}{2}\pi} J_1 (m \cos \phi) \cos^2 \phi \, d\phi = \sqrt{\left(\frac{\pi}{2m}\right)} J_{\frac{3}{2}} (m) = \frac{\sin m}{m^2} - \frac{\cos m}{m}, \qquad (6)$$

so that

$$P = -(K-1) \ 4\pi R^3 \ e^{i(nt-kr)} \left(\frac{\sin m}{m^3} - \frac{\cos m}{m^2}\right), \qquad (7)$$

in agreement with (5)   The secondary disturbance vanishes with P, viz., when $\tan m = m$, or

$$m = 2kR \cos \tfrac{1}{2}\chi = \pi \,(1\,4303,\ 2\,4590,\ 3\,4709,\ 4\,4747,\ 5\,4818,\ \text{etc})\dagger \quad (8)$$

The smallest value of kR for which P vanishes occurs when $\chi = 0$, *ie* in the direction *backwards* along the primary ray   In terms of λ the diameter is

$$2R = 0\,715\lambda. \qquad (9)$$

In directions nearly along the primary ray *forwards*, $\cos \tfrac{1}{2}\chi$ is small, and evanescence of P requires much larger ratios of R to λ.   As was formerly fully discussed, the secondary disturbance vanishes, independently of P, in the direction of primary vibration ($a = 0, \beta = 0$)

In general, the intensity of the secondary disturbance is given by

$$f_1^2 + g_1^2 + h_1^2 = \left(\frac{k^2 P_0}{4\pi r}\right)^2 \left(1 - \frac{\gamma^2}{r^2}\right), \qquad (10)$$

in which P_0 denotes P with the factor $e^{i(nt-kr)}$ omitted, and is a function of χ, the angle between the secondary ray and the axis of x If we take polar co-ordinates (χ, ϕ) round the axis of x,

$$1 - \frac{\gamma^2}{r^2} = 1 - \sin^2 \chi \, \cos^2 \phi , \qquad (11)$$

and the intensity at distance r and direction (χ, ϕ) may be expressed in terms of these quantities   In order to find the effect upon the transmitted light, we have to integrate (10) over the whole surface of the sphere r Thus

$$r^2 \iint \sin \chi \, d\chi \, d\phi \,(f_1^2 + g_1^2 + h_1^2) = \pi \int_0^\pi \sin \chi \, d\chi \left(\frac{k^2 P_0}{4\pi}\right)^2 (1 + \cos^2 \chi)$$

$$= \pi k^4 (K-1)^2 R^6 \int_0^\pi \sin \chi \, d\chi \,(1 + \cos^2 \chi) \frac{(\sin m - m \cos m)^2}{m^6}$$

$$= \tfrac{1}{2}\pi k^3 R^4 (K-1)^2 \int_0^{2kR} \frac{dm}{m^5} \left\{ 2 - \frac{m^2}{k^2 R^2} + \frac{m^4}{4k^4 R^4} \right\}$$

$$\times \{1 + m^2 + (m^2 - 1) \cos 2m - 2m \sin 2m\}. \qquad (12)$$

[*] 'Lond Math Soc. Proc.,' vol 25, p 71 (1893)
[†] See 'Theory of Sound,' § 207

The integral may be expressed by means of functions regarded as known Thus on integration by parts

$$\int_0^m \{1 + m^2 + (m^2 - 1)\cos 2m - 2m \sin 2m\}\frac{dm}{m^5}$$

$$= -\frac{1 - \cos 2m}{4m^4} + \frac{\sin 2m}{2m^3} - \frac{1}{2m^2} + \frac{1}{2},$$

$$\int_0^m \{1 + m^2 + (m^2 - 1)\cos 2m - 2m \sin 2m\}\frac{dm}{m^3}$$

$$= -\frac{1}{2m^2} + \int_0^m \frac{1 - \cos 2m}{m} dm + \frac{\cos 2m}{2m^2} + \frac{\sin 2m}{m} - 1,$$

$$\int_0^m \{1 + m^2 + (m^2 - 1)\cos 2m - 2m \sin 2m\}\frac{dm}{m}$$

$$= \int_0^m \frac{1 - \cos 2m}{m} dm + \frac{m^2}{2} + \frac{m \sin 2m}{2} + \frac{5 \cos 2m}{4} - \frac{5}{4}$$

Accordingly, if m now stand for $2kR$, we get

$$r^2 \iint \sin \chi \, d\chi \, d\phi \, (f_1^2 + g_1^2 + h_1^2)$$

$$= \frac{\pi R^2 (K - 1)^2}{8} \left\{ -\frac{7(1 - \cos 2m)}{2m^2} - \frac{\sin 2m}{m} + 5 + m^2 \right.$$

$$\left. + \left(\frac{4}{m^2} - 4\right)\int_0^m \frac{1 - \cos 2m}{m} dm \right\} \quad (13)$$

If m is small, the { } in (13) reduces to

$$0 + 0 \times m^2 + \tfrac{4}{27} m^4,$$

so that ultimately

$$(13) = \tfrac{8}{27} \pi k^4 R^6 (K - 1)^2, \tag{14}$$

in agreement with the result which may be obtained more simply from (5) If we include another term, we get

$$(13) = \tfrac{8}{27} \pi k^4 R^6 (K - 1)^2 \left(1 - \frac{2k^2 R^2}{5}\right) \tag{15}$$

As regards the definite integral, still written as such, in (13), we have

$$\int_0^m \frac{1 - \cos 2m}{m} dm = \int_0^{2m} \left\{\frac{x}{1.2} - \frac{x^3}{4!} + \frac{x^5}{6!} - \dots\right\} dx = \gamma + \log(2m) - \text{Ci}(2m),$$

$$\tag{16}$$

where γ is Euler's constant (0 5772156) and Ci is the cosine-integral, defined by

$$\text{Ci}(x) = \int_\infty^x \frac{\cos u}{u} du \tag{17}$$

As in (16), when x is moderate, we may use

$$\mathrm{Ci}(x) = \gamma + \log x - \tfrac{1}{2}\frac{x^2}{1 \cdot 2} + \tfrac{1}{4}\frac{x^4}{1 \cdot 2 \cdot 3 \cdot 4} - \ldots,\qquad (18)$$

which is always convergent When x is great, we have the semi-convergent series

$$\mathrm{Ci}(x) = \sin x\left\{\frac{1}{r} - \frac{1 \cdot 2}{x^3} + \frac{1 \cdot 2 \cdot 3 \cdot 4}{x^5} - \right\}$$
$$- \cos x\left\{\frac{1}{x^2} - \frac{1 \cdot 2 \cdot 3}{x^4} + \frac{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5}{x^6} - \right\}\qquad (19)$$

Fairly complete tables of $\mathrm{Ci}(x)$, as well as of related integrals, have been given by Glaisher [*]

When m is large, $\mathrm{Ci}(2m)$ tends to vanish, so that ultimately

$$\int_0^m \frac{1 - \cos 2m}{m}\,dm = \gamma + \log(2m)$$

Hence, when $k\mathrm{R}$ is large, (13) tends to the form

$$(13) = \tfrac{1}{2}\pi k^3 \mathrm{R}^4 (\mathrm{K} - 1)^2 \qquad (20)$$

Glaisher's Table XII gives the maxima and minima values of the cosine-integral, which occur when the argument is an odd multiple of $\tfrac{1}{2}\pi$ Thus—

n	$\mathrm{Ci}(n\pi/2)$	n	$\mathrm{Ci}(n\pi/2)$
1	+0 4720007	7	−0 0895640
3	−0 1984076	9	+0 0700653
5	+0 1237723	11	−0 0575011

These values allow us to calculate the { } in (13), viz,

$$-\frac{7(1 - \cos 2m)}{2m^2} - \frac{\sin 2m}{m} + 5 + m^2 + \left(\frac{4}{m^2} - 4\right)[\gamma + \log 2m - \mathrm{Ci}(2m)],\quad (21)$$

when $2m = n\pi/2$, and n is an odd integer In this case $\cos 2m = 0$ and $\sin 2m = \pm 1$, so that (21) reduces to

$$-\frac{56}{n^2\pi^2} \pm \frac{4}{n\pi} + 5 + \frac{n^2\pi^2}{16} + \left(\frac{64}{n^2\pi^2} - 4\right)[\gamma + \log(n\pi/2) - \mathrm{Ci}(n\pi/2)]\qquad (22)$$

We find

n	(22)	n	(22)
1	0 0530	7	23 440
3	2 718	9	42 882
5	10 594	11	65 956

* 'Phil Trans,' vol. 160, p. 367 (1870).

For values of n much greater, (22) is sufficiently represented by $n^2\pi^2/16$, or m^2, simply It appears that there is no tendency to a falling-off in the scattering, such as would allow an increased transmission

In order to make sure that the special choice of values for m has not masked a periodicity, I have calculated also the results when n is even Here $\sin 2m = 0$ and $\cos 2m = \pm 1$, so that (21) reduces to

$$-\frac{112\,(1\text{ or }0)}{n^2\pi^3}+5+\frac{n^2\pi^2}{16}+\left(\frac{64}{n^2\pi^2}-4\right)[\gamma+\log{(n\pi/2)}-\mathrm{Ci}\,(n\pi/2)] \quad (23)$$

The following are required —

n	$\mathrm{Ci}\,(n\pi/2)$	n	$\mathrm{Ci}\,(n\pi/2)$
2	$+0\ 0738$	8	$-0\ 0061$
4	$-0\ 0224$	10	$+0\ 0040$
6	$+0\ 0106$		

of which the first is obtained by interpolation from Glaisher's Table VI, and the remainder directly from (19) Thus —

n	(23)	n	(23)
2	0 7097	8	32 336
4	6 1077	10	53 477
6	16 156		

The better to exhibit the course of the calculation, the actual values of the several terms of (23) when $n = 10$ may be given We have

$$-\frac{112}{n^2\pi^2}=-0\ 11348, \qquad \frac{n^2\pi^2}{16}=61\ 685,$$

$$4-\frac{64}{n^2\pi^2}=4-0\ 06485=3\ 93515,$$

$$\gamma+\log{(\pi/2)}+\log{n}-\mathrm{Ci}\,(n\pi/2)=0\ 57722+0\ 45158+2\ 30259-0\ 0040$$
$$=13\ 094,$$

so that

$$\left(4-\frac{64}{n^2\pi^2}\right)\{\gamma+\log{(n\pi/2)}-\mathrm{Ci}\,(n\pi/2)\}=13\ 094$$

It will be seen that from this onwards the term $n^2\pi^2/16$, viz, m^2, greatly preponderates, and this is the term which leads to the limiting form (20).

The values of $2R/\lambda$ concerned in the above are very moderate. Thus, $n = 10$, making $m = 4\pi R/\lambda = 10\pi/4$, gives $2R/\lambda = 5/4$ only. Neither

below this point, nor beyond it, is there anything but a steady rise in the value of (13) as λ diminishes when R is constant. *A fortiori* is this the case when R increases and λ is constant.

An increase in the light scattered from a single spherical particle implies, of course, a decrease in the light directly transmitted through a suspension containing a given number of particles in the cubic centimetre The calculation is detailed in my paper "On the Transmission of Light through an Atmosphere containing Small Particles in Suspension,"[*] and need not be repeated It will be seen that no explanation is here arrived at of the augmentation of transparency at a certain stage observed by Keen and Porter The discrepancy may perhaps be attributed to the fundamental supposition of the present paper, that the relative index is very small, a supposition not realised when sulphur and water are in question But I confess that I should not have expected so wide a difference, and, indeed, the occurrence of anything special at so great diameters as 10 wave-lengths is surprising

One other matter may be alluded to It is not clear from the description that the light observed was truly transmitted in the technical sense This light was much attenuated—down to only 5 per cent Is it certain that it contained no sensible component of scattered light, but slightly diverted from its original course ? If such admixture occurred, the question would be much complicated

[*] 'Phil Mag,' vol 47, p 375 (1899), 'Scientific Papers,' vol 4, p 397

The Rate of Solution of Hydrogen by Palladium

By Alfred Holt, M A , D Sc

In two recent communications* the view has been advanced that in hydrogen-palladium the dissolved gas cannot be regarded as homogeneously distributed, and that solution takes place through the medium of an amorphous metallic phase which acts as a vehicle for the transference of gas to the crystalline metal   Experiments have been described from which it is concluded that in hydrogen-palladium one is dealing with a case of simultaneous adsorption and solution (or sorption), since as soon as any gas is adsorbed solution begins through diffusion from the adsorbed layer

The adsorption equilibrium would be rapidly established, too quickly, perhaps, for any record of its rate to be measured, but could such observations be made it might be expected that the following relation would hold —

$$dc/dt = kC^n,$$

where C is the concentration in the adsorbed layer and k and n constants depending on the nature of the adsorbent and the substance adsorbed, the rate of adsorption of a gas at constant pressure varying with the concentration of the gas in the adsorbed layer. If, therefore, the adsorbed layer is maintained at constant concentration by surrounding it with an unlimited supply of gas at constant pressure, the rate of inward diffusion from it could be measured   Thus a complete rate of solution curve should consist of two portions, the first representing adsorption and the second inward diffusion, the two coinciding when the rate of adsorption equals the rate of diffusion

Should there be no adsorption, or should the dispersivity be so great that the metal may be regarded entirely as surface, then only one phenomenon would be present, and a curve representing the rate of solution of gas should show no discontinuity of curvature   It might, of course, be impossible to observe the changes of rate with concentration for the initially adsorbed gas, since adsorption is usually regarded as an exceedingly rapid process, and

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* Holt, Edgar, and Firth, 'Zeit Phys Chem ,' vol. 82, p 5 (1913), and Andrew and Holt, 'Proc Roy Soc,' A, vol 89, p 170 (1913).

hence a smooth rate-concentration curve need not necessarily imply the absence of all but one phenomenon

It has already been mentioned that there is evidence that solution of gas takes place through the intermediary of an allotropic and probably amorphous phase of the metal   The solubility of hydrogen in this phase (which throughout this paper will be called α-palladium, the other phase being called β-palladium) may be far more rapid than in the stable β-variety, though the solubility of hydrogen in the two forms may be nearly the same. Were this the case, then a rate-concentration curve should at first give values for the solution in α-palladium until this rate had decreased to and equalled that in the β-modification, the subsequent portion of the curve representing the change of concentration per unit time in this latter form of the metal.

The graphs obtained under these conditions would resemble in their general form those for simultaneous adsorption and solution, except that the first portion of the curve would be more drawn out, since it is highly improbable that saturation of α-palladium would take place as rapidly as true adsorption   There is, however, no real distinction except in degree between the two cases.   If one imagines the α-metal as a film on a mass of the β-form, then if the rate of solution of gas in α- and β-palladium is very different, the phenomenon of adsorption might be simulated

In the present communication an attempt has been made to determine the rate of solution-concentration curves for hydrogen at constant pressure in different forms of palladium and under different conditions, in order to investigate further the phenomenon of the solution of hydrogen in this metal The apparatus employed is illustrated in fig 1.

The palladium was contained in the bulb A which, by means of the three-way tap B, could be put into communication either with the pump, or with the supply of hydrogen, or with the long tube CD, which ended in the
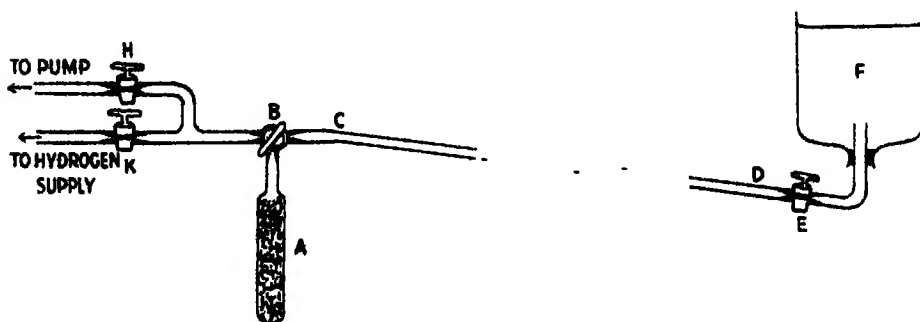
FIG. 1

reservoir F, and was filled with a liquid paraffin of low vapour pressure The tube CD had a uniform bore of about 4 mm, and was somewhat more than 400 cm in length It was graduated throughout its entire length, and was somewhat raised at one end so as to ensure a sharp meniscus to the liquid running up it.

The method of conducting an experiment was as follows ·—A weighed amount of metal was sealed in the bulb A, and, the reservoir F being empty, the air through the apparatus was at atmospheric pressure The tap K was then closed, and B turned so as to permit the evacuation of the space HKB by the pump This being accomplished B was further turned, and the dead space in A evacuated, its volume being determined by reducing the collected gas to N T P The taps H and B being now shut, hydrogen was allowed to fill the space HKB, A meanwhile remaining evacuated The reservoir F being now filled with liquid, E was opened, and a stream of hydrogen passed through CD for several hours so as to displace completely the air it contained Finally the tap K was shut, and the position of the liquid in CD being noted on the scale, B was turned so as to place the metal in contact with the gas in CD

The liquid at once moved rapidly along the scale on account of the vacuum in A, but the volume of the dead space having been determined in terms of scale divisions along CD, the point at which readings of the rate of solution could be commenced was at once ascertainable

The rate measured was the time taken by the liquid to travel one division on the scale, and determinations were made throughout its length at points representing known concentrations of gas in the metal. The gas was maintained at an almost constant pressure during the experiment, since the diameter of the reservoir F was so great that the total volume of liquid required to fill the tube CD did not alter the surface level by more than a few millimetres, and the specific gravity of the paraffin employed being somewhat less than that of water, the small apparent error arising from changes in the level of the liquid in F was diminished.

The solution of gas in the metal caused a rise of temperature in A which operated in two ways, on the one hand hastening the rate of occlusion by heating the metal, on the other hand expanding the gas in A and causing a check to the rate at which the liquid would travel along CD The former of these effects was obviated as far as possible by placing A in a water-bath at constant temperature, while the latter was rendered quite negligible by making the dead space in A so small in comparison to the volume of CD that any expansion of the small volume would have no material effect on the total volume of gas in the apparatus

A further source of error might arise from the viscosity of the liquid causing a lag in the rate of its advance along the scale during a period of rapid occlusion of gas   Some experiments were therefore carried out with different liquids, but though the viscosity has an undoubted effect in any one experiment, it caused little error in the relative values of a series.

The following tables contain a summary of the results obtained with palladium black, very thin foil 0 004 mm , and foil about 0 2 mm thick

Table I —Palladium Black   Temperature 15° C

(1)		(2)	
Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale
	secs		secs
112	0 3	112	0 3
162	0 6	162	0 6
212	1 6	212	1 3
232	2 8	262	3 2
252	4 2	282	4 5
272	8 6	312	11 0
292	21 ·0	332	32 0
312	48 0		

Table II —Foil 0 004 mm thick

Temperature 15° C				Temperature 83° C	
(1)		(2)		(3)	
Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale
	secs		secs		secs
11	3 0	5	1 0	11	0 6
22	4 6	22	4 0	33	1 4
33	5 ·6	33	4 8	55	1 8
55	6 ·6	55	6 2	77	2 4
88	7 ·0	88	10 ·0	99	2 5
121	7 4	99	11 6	121	3 2
143	8 0	110	15 ·0	143	4 4
176	8 2	121	19 0	165	6 ·0
209	9 ·0	132	23 0	187	8 ·0
220	9 6			209	13 5
242	10 ·6				
264	13 6				
286	16 0				
306	23 ·0				
330	37 0				

Table III —Foil about 0·2 mm thick

Temperature 15° C						Temperature 70° C	
(1)		(2)		(3)		(4)	
Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale
	secs		secs		secs		secs
40	8 0	40	13 ·0	40	32 8	40	6 4
74	8 6	74	13 2	74	56 ·0	74	7 2
108	10 4	108	14 0	108	67 4	142	7 6
142	12 4	176	15 6	142	76 4	176	8 2
210	15 0	210	16 8	176	88 ·0	210	9 2
244	16 0	244	18 4	210	95 0	244	9 4
278	16 9	278	19 2			278	10 6
312	17 ·9	312	20 4			312	12 6
346	19 4	346	23 0			346	14 0
380	22 4	380	25 8			380	15 8
414	25 5	414	29 4			414	18 4
482	39 6					448	22 6
						516	41 0

Table IV —Foil about 0·2 mm thick

Metal cooled in hydrogen after heating *in vacuo.*		Metal cooled in hydrogen after heating in hydrogen	
Volume of gas occluded by 1 vol of metal	Time for one division of scale	Volume of gas occluded by 1 vol of metal	Time for one division of scale
	secs		secs
40	4 2	6	5 8
74	4 4	40	5 ·6
108	6 8	74	14 2
176	12 6	108	76 0
210	22 ·0	123	108 0
244	28 4		
278	32 0		
312	33 4		
346	37 6		
380	42 2		
414	47 0		

By the use of the metal in different states it was hoped that any effect due to variation of dispersivity might be detected, while palladium black served also to form a comparison between α- and β-metal, since the black was believed to consist mainly of the α-form

In the preceding tables only one specimen of palladium black and thick or

thin foil was employed for the various experiments with each form of the metal

The data contained in the above tables are represented by graphs in figs 2, 3, 4, and 5, which correspond with Tables I, II, III, and IV respectively, but for convenience in arranging the curves the values for Nos 2 and 3 in fig 3

Vol. of gas occluded by 1 vol of metal
Fig 2
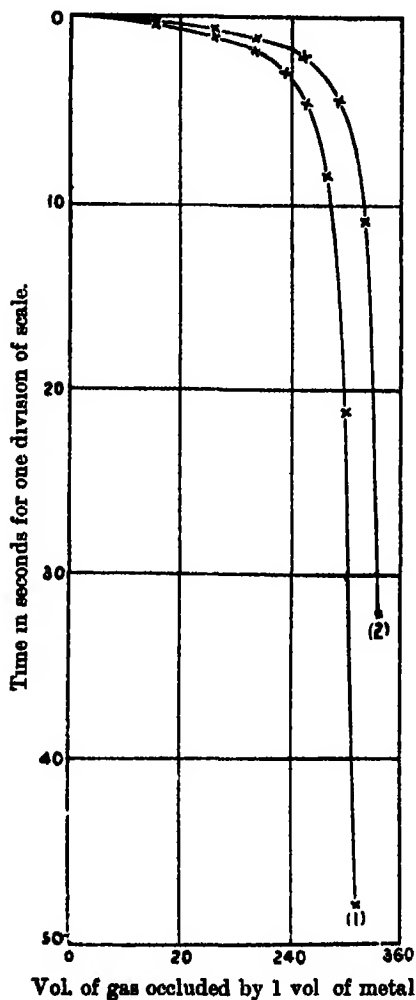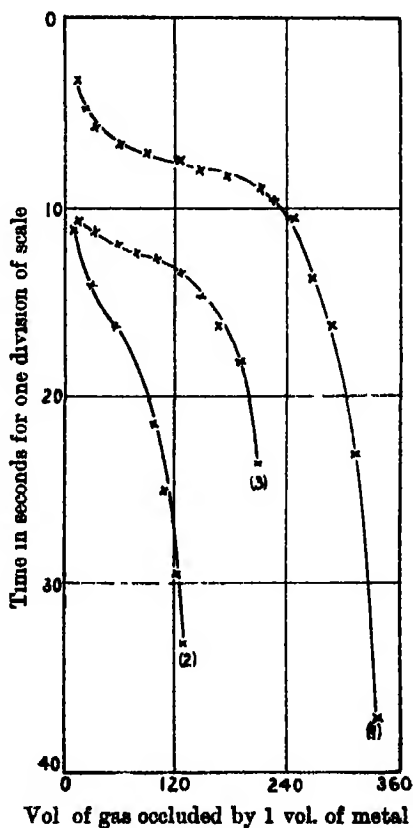
Vol of gas occluded by 1 vol. of metal
Fig. 3.

have been increased in each case by 10 seconds above the times in Table II, while No. 3, fig. 4, is plotted in half values

An examination of these graphs shows that at ordinary temperatures (15° C) there is, except in the case of palladium black, a more or less

pronounced deflection of the curve, not, however, always coinciding with a constant concentration of gas in the metal

The curves may be considered as composite, two of similar general form being partially superimposed   Thus in the case of thin foil the initial portion may be taken to represent the region where the first curve merges into
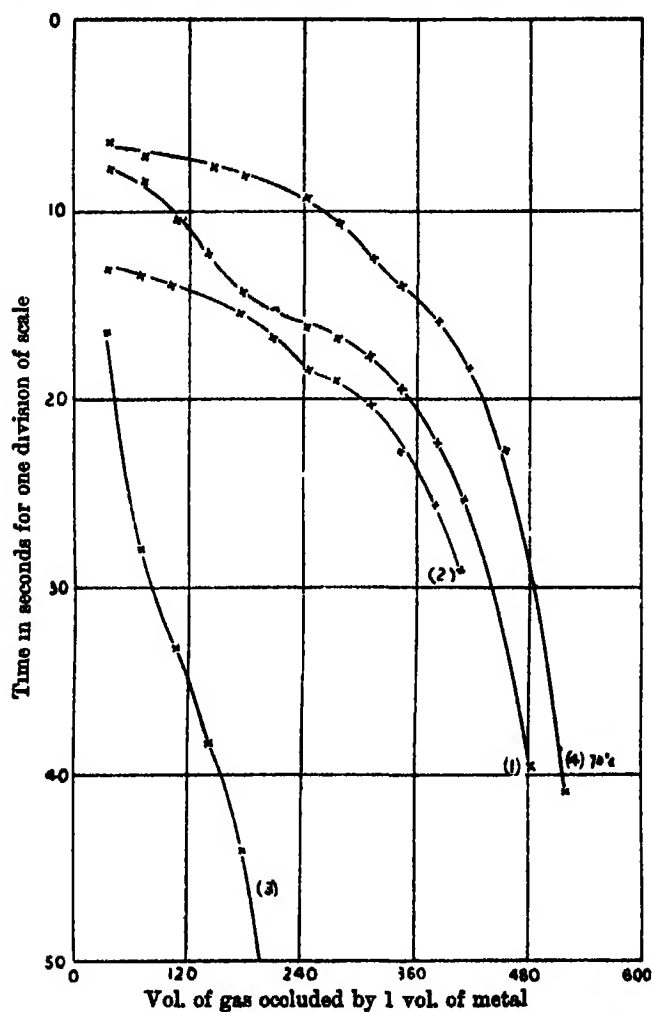
Fig 4

the second, the graph consisting almost entirely of this latter, whilst for thick foil, the break between the two curves occurs more towards the centre of the figure

It could, perhaps, be argued that the change of curvature is so slight that it might well arise from errors in observation, but against this view must be

set the fact that no deflection occurs with palladium black, whereas with the other forms of the metal there is no curve but exhibits it to some extent

These curves cannot be expressed by any simple formula, but the relation-
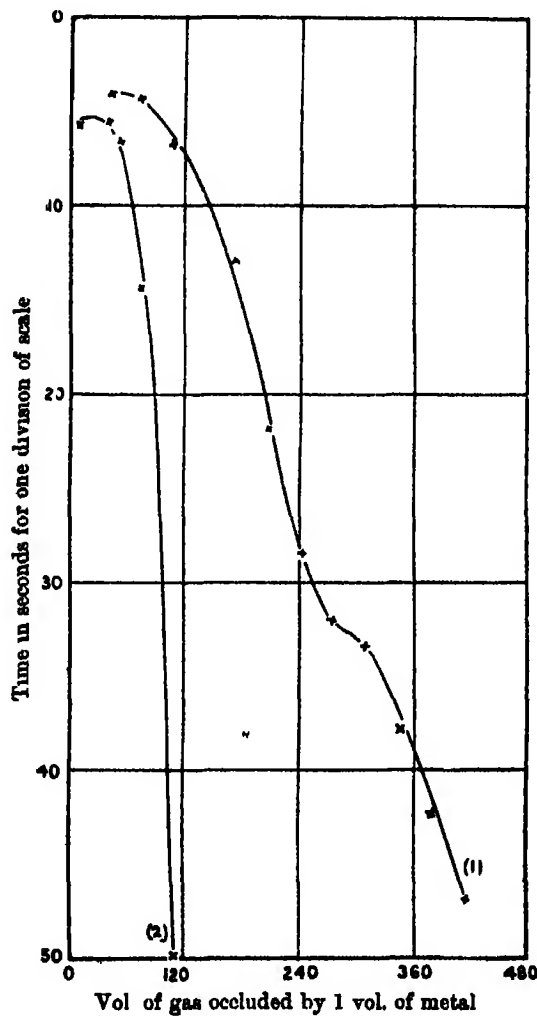
Fɪɢ. 5.

ship between the rate of occlusion and the total concentration of gas in the metal appears in general to be represented by such an expression as

$$dc/dt = KC^n$$

where n is not a constant, but varies as a function of C Neither has n a constant value for any particular form of the metal, for in the tables of rate

values given above it is seen that with the same specimen of metal very
different rates are obtained

This variation of rate for the same sample of palladium is no new observa-
tion, but taken in conjunction with the fact that n in the above expression
varies also with C, precludes the possibility of representing the curves by any
simple expression which has a definite physical meaning

Since n is not a constant, no information as to the molecular condition
of the dissolved gas is obtained from the rate of solution values, but the view
of Travers and Zacharias that one is really dealing with a diffusion column
appears to receive support   The phenomena can be imagined as follows —
Initially, a certain amount of condensation on the exterior of the metal may
take place very rapidly, far too quickly, indeed, to be detected by the methods
employed in this investigation   The surface of the metal possessing, how-
ever, a very porous and irregular structure, an appreciable time would be
taken by the gas to diffuse into its interstices, this diffusion representing the
initial portion of the curves for palladium foil   Since, however, after a
sufficiently long time has elapsed, gas is found in the interior of the metal,
it must be assumed that a more intimate kind of solution must take place
immediately beneath the surface   Here the gas would no longer be merely
penetrating into the fissures between metallic grains but would be actually
entering the grains themselves, passing into solution, for solution and intra-
molecular diffusion in such a case as this are the same   This would represent
the second portion of the rate of solution curves

For convenience, we may call the initial phenomenon surface diffusion and
associate it with α-palladium, and the second solution in the β-metal, and in
both cases the rate would diminish with increasing total concentration of gas
in the metal, since the smaller and more sinuous the passages became into
which the gas was passing, the longer would be the time taken, and to the
diffusion effects would be added those of transpiration   A simple logarithmic
relation between the rate of solution and concentration of gas within the
metal could therefore hardly be expected

Any attempt to explain the observed phenomena of the rate of solution
must, however, take cognisance of the fact that, so far as is known, the
pressure-temperature concentration 'relations of hydrogen in palladium do
not greatly change with different forms of the metal (the experiments of Paal
and Gerum[*] on colloidal palladium excepted), and that palladium black is
always active towards hydrogen, whereas the stable condition of the crystalline
metal is nearly inactive   If, however, to the hypothesis of surface diffusion

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[*] 'Ber,' vol 41, p. 805 (1908)

and solution is added that of an α- and β-form of the metal, the observed phenomena can be explained

In order to account for the constancy of the temperature-pressure-concentration relations, it must be assumed that to each molecule of metal can be associated a certain definite quantity of hydrogen, such quantity varying with the pressure and temperature of the gas   The gas may be regarded as a skin on the metallic particles.   Now, if these particles are arranged haphazard, it will be far easier for the gas to diffuse among them and saturate them than if the particles were close packed in some crystalline orientation   In palladium black, which is believed to be amorphous, the particles probably possess little regular arrangement, so the most favourable condition for rapid saturation is presented, and, unless the particles become close packed through crystallisation, there is no reason why the activity or power of rapid saturation of the metal should diminish The more completely crystalline the metal, the greater should be the difficulty experienced by the gas in entering it, a fact of common observation , α-palladium is therefore imagined as the form with the least regularly orientated and close-packed particles, β-palladium being truly holocrystalline, but the actual phenomenon of solution is the same in either case

If in palladium black the particles are loosely and irregularly arranged, there would be little, if any, distinction between surface condensation and intramolecular diffusion, the interstices of the surface becoming narrower and narrower and more and more sinuous, till they became spaces between irregularly arranged metallic particles   Hence a rate of solution curve should show no break

When, however, the gas, after condensing in the surface irregularities, finds itself in contact with metal, the particles of which are in the main close packed, the rate of diffusion would change.

It appears from a large number of experiments that the deflection of the rate curve occurs almost invariably after the metal has been exposed to the gas for about the same interval of time, and that it does not depend on the amount of gas already dissolved   In a series of nine experiments with thick foil, in which the rate of solution varied greatly from one experiment to the next, the time interval before the deflection was found to vary from 13 to 16 minutes, with a mean value of about 15 minutes   Assuming the view that solution of gas depends on the primary saturation of α-palladium, it must be concluded that, after about a quarter of an hour, the rate of solution of gas by the α-form equals the rate at which β-palladium receives gas by diffusion from that variety   If the α-phase was uniformly exposed to the gas at constant pressure, it would acquire a definite saturation in a definite

time, quite irrespective of the amount of phase present, for the actual volume of gas absorbed would increase in direct proportion to the amount of the α-phase.

It is improbable that thermal effects arising from the condensation of the hydrogen have any marked effect under the conditions of the experiment, as, owing to the fact that the bulb containing the metal was kept in circulating cold water, its temperature scarcely rose except during the first two or three minutes

Turning now to the curves in which the metal was allowed to cool in hydrogen, two distinct types are observed, according as the metal had previously been heated, either *in vacuo* or in the gas   When the metal which has been heated *in vacuo* to a dull red heat, and to which hydrogen has been admitted at this temperature, is allowed to cool in the gas, curves very similar to those already described are obtained.   A deflection in this curve has always been observed   When, however, the metal, after previous saturation with hydrogen, is heated and then allowed to cool in the gas, there is no indication in the rate of solution curve of any irregularity   The rate falls extremely rapidly, though after a long enough interval of time the same amount of gas may in each case be retained by the metal

The hypothesis already put forward provides an explanation of this difference in behaviour   When the metal is heated in the gas, after initial saturation in the cold, hydrogen is evolved, but the palladium still remains saturated, the solubility of gas decreasing with rise of temperature, so that, when the metal is allowed to cool, it is already saturated, though the actual volume of dissolved gas is but small   It appears probable that this gas is dissolved in the β-metal, for on cooling either this saturated palladium, or metal to which hydrogen has been admitted at a dull red heat, the initial portions of the solution curve are very similar, and are characterised by a rapid diminution of rate.   Now in this latter case the solution curve again shows a deflection, the phenomena being the same as during solution in the cold, where the α-phase is the initial solvent

The full cycle of the solution phenomena during heating and cooling may be imagined thus   Palladium in the cold first dissolves gas in its α-, and then in its β-phase   Eventually there is complete saturation.   On heating, gas is evolved though the metal remains saturated as regards the β-phase   Solution again occurs in the α-phase on cooling, but the metal already containing a large volume of gas, the diffusion from the α- to the β-phase is so slow that it does not produce any marked irregularity in the rate curve   When, however, hydrogen is initially admitted to the hot metal solution first takes place in the α- and subsequently in the β-phase exactly as during solution in the cold.

If diffusion from the α- to the β-phase is slow under even favourable circumstances, it follows that if the β-phase already contains gas the rate may become almost unmeasurable, for, as has been shown in this communication, a small change of concentration may produce a great change in the rate of solution

There appears, therefore, every reason to suppose that the solution of hydrogen by palladium is a phenomenon quite analogous to the cases of sorption of gases by other solids, such as charcoal and celluloid, which have already been examined by various authors

Conclusion

The rate of solution of hydrogen by palladium is not a simple function of the concentration of gas in the metal   The rate curves consist of two portions (except in the case of palladium black), which have been interpreted as referring to solution in two different forms of the metal The smooth rate curve for palladium black is taken to mean the almost complete absence of one of these forms

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Note on a Functional Equation employed by Sir George Stokes

By Sir James Stirling, F.R.S

1 In a paper by Sir George Stokes "On the Intensity of the Light Reflected from or Transmitted through a Pile of Plates,"[*] the author forms and solves two functional equations, viz —

$$\phi(m+n) = \phi(m) + \frac{\phi(n)\{\psi(m)\}^2}{1-\phi(m)\phi(n)}, \tag{1}$$

$$\psi(m+n) = \frac{\psi(m)\psi(n)}{1-\phi(m)\phi(n)}. \tag{2}$$

The symbols m, n represent, as was required by the object of the paper, positive integers, but in the course of the investigation he deals with them as continuous variables, solves the equations (1) and (2) on that footing, and finally verifies the equations when m, n are integers   The two equations are treated as independent, and the results are thus expressed,

$$\frac{\phi(m)}{\sin m\beta} = \frac{\psi(m)}{\sin \alpha} = \frac{1}{\sin(\alpha+m\beta)}, \tag{3}$$

[*] Published in 'Roy. Soc Proc.' for 1862 , see his 'Math and Phys. Papers,' vol. 4, pp. 145, 148, 149

where α, β are constants.   In what follows m, n will be taken to be ordinary continuous variables.

2. The main object of the paper 'of Sir George Stokes is physical, not mathematical, and the purpose of the present note is to call attention to some mathematical points not explicitly dealt with by him, viz :—

(*a*) The two functional equations are not independent, equation (2) being capable of being deduced from equation (1),

(*b*) The results (3) may be arrived at from equation (1) *alone*, and constitute the general solution of that equation.   No such general solution of equation (2) has been obtained

3. If equation (1) be differentiated with respect to n, the result, after some obvious reductions, is

$$\phi'(m+n) = \phi'(n)\,\{\psi(m)\}^2/\{1-\phi(m)\phi(n)\}^2. \tag{4}$$

If m and n be interchanged in the last equation, the result is

$$\phi'(m+n) = \phi'(m)\,\{\psi(n)\}^2/\{1-\phi(m)\phi(n)\}^2, \tag{5}$$

so that $\qquad \{\psi(m)\}^2/\phi'(m) = \{\psi(n)\}^2/\phi'(n) = A$, a constant,

or $\qquad\qquad\qquad \{\psi(m)\}^2 = A\phi'(m). \tag{6}$

Hence $\qquad \{\psi(m+n)\}^2 = A\phi'(m+n),$

[by (4)] $\qquad\qquad = A\phi'(n)\,\{\psi(m)\}^2/\{1-\phi(m)\phi(n)\}^2$

[by (6)] $\qquad\qquad = \{\psi(n)\}^2\{\psi(m)\}^2/\{1-\phi(m)\phi(n)\}^2,$

and therefore $\qquad \psi(m+n) = \pm\dfrac{\psi(m)\,\psi(n)}{1-\phi(m)\phi(n)},$

which is equation (2), with an ambiguity of sign   This ambiguity also arises in the course of Sir George Stokes' investigation and is dealt with by him.

It follows that every value of $\phi(m)$, $\psi(m)$, which satisfies equation (1) satisfies also equation (2); but it is not necessarily true that every value of $\phi(m)$, $\psi(m)$, which satisfies equation (2) also satisfies equation (1)

4 If now in equation (1), and that derived from it by interchanging m, n, there be substituted for $\{\psi(m)\}^2$, $\{\psi(n)\}^2$, their values $A\phi'(m)$, $A\phi'(n)$, it appears that

$\phi(m) + \phi(n)\,A\phi'(m)/\{1-\phi(m)\phi(n)\}$

$\qquad\qquad\qquad = \phi(n) + \phi(m)\,A\phi'(n)/\{1-\phi(m)\phi(n)\},$

which, when multiplied on both sides by $1-\phi(m)\phi(n)$, becomes

$\phi(m)\{1-\phi(m)\phi(n)\} + A\phi'(m)\phi(n) = \phi(n)\{1-\phi(m)\phi(n)\} + A\phi(m)\phi'(n),$

or

$\phi(m)\{1-A\phi'(n)\} - \phi(n)\{1-A\phi'(m)\} - \phi(m)\phi(n)\{\phi(m)-\phi(n)\} = 0,$

or, finally, $\dfrac{1-A\phi'(n)}{\phi(n)}+\phi(n)-\left\{\dfrac{1-A\phi'(m)}{\phi(m)}+\phi(m)\right\}=0,$

whence $\dfrac{1-A\phi'(m)}{\phi(m)}+\phi(m) = $ a constant,

which (after Sir G Stokes) may be written $2\cos\alpha$, and consequently

$$\phi'(m) = A^{-1}[\{\phi(m)\}^2-2\cos\alpha\,\phi(m)+1], \tag{7}$$

a differential equation identical in form with that ultimately arrived at by Stokes, his constant β standing for $A^{-1}\sin\alpha$ * The results (3) are obtained by integrating this equation. A fresh constant is thus introduced, and its value is to be found by ascertaining the value of $\phi(0)$. If in equation (1) the value 0 is assigned to n, it appears that

$$0 = \phi(0)\{\psi(m)\}^2/\{1-\phi(m)\phi(0)\},$$

whatever m may be, and consequently, *in general*, the value of $\phi(0)$ is zero

The results (3) are thus deduced from equation (1) alone, without recourse to equation (2)

5 The solution of the two functional equations was proposed by Sir George Stokes in a Smith's Prize Examination Paper for 1860,† and was introduced as an example into Boole's 'Finite Differences', but the values of $\phi(x)$ and $\psi(x)$ given in that work are deficient in generality. This defect, it is right to say, is not attributable to the late Professor Boole

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* See 'Math. and Phys Papers,' vol 4, p. 149, equation (10)
† See 'Math and Phys Papers,' vol 5, p. 334, Question 14

A Determination of the Electromotive Force of the Weston Normal Cell in Semi-absolute Volts

By A Norman Shaw, M Sc, 1851 Exhibitioner and King Research Fellow of McGill University, Montreal

(Abstract)

Accounts of several absolute determinations of current have been published in recent years, but the agreement between the various results has not been quite as close as the accuracy of the work demanded This paper presents the result of a determination performed with the aid of a modified form of the bifilar Weber electro-dynamometer As this instrument has not been employed in any of the recent determinations, the result has the force of a determination by a new method The former obstacles to a precise use of this type of dynamometer have been overcome, and it is claimed that the absolute accuracy of the value of the electromotive force of the normal Weston standard cell has been considerably increased by this investigation

The electro-dynamometer was constructed by Nalder, but several fundamental changes have been made in its design It was originally set up by Mr R. O King under the direction of Prof H L Callendar, and the work by King has been fully described by Callendar, who made important changes in the design of the instrument at that time * Preliminary observations were obtained by R O King for the electromotive force of the old Board of Trade form of crystal Clark cell, and it was intended that more accurate work should be obtained later. It was suggested by Prof Barnes that the writer should complete this investigation, and through the generosity of Mr R. O. King, a Fellowship was provided which enabled him to devote a year almost without interruption to the research

The paper is divided into the following sections —

Preface by Prof H L Callendar, F R S

I Introduction

II The Theory of the Electro-dynamometer

III The Dimensions of the Fixed Coils

IV The Ratio of the Radii of the Fixed and Suspended Coils The Dimensions of the Suspended Coils

V. The Calculation of the Dynamometer Constants

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* Callendar, 'Phil Trans,' A, vol 199, p 55 (1902)

In the second section the general theory of the instrument is developed and the formulæ which may be applied in its use are given   It is explained how certain sources of error which appeared in the early use of electro-dynamometers have been eliminated

The third section gives an account of the original determination of the mean radius of the fixed coils and also the method of obtaining the mean distance between the planes of the fixed coils

The theory and method of measuring the mean radius of the small coils by electromagnetic comparison with the large coils is outlined in the fourth section   This is one of the most difficult parts of the investigation and nearly 400 observations for various quantities are involved in the final mean   It is thought that an accuracy of one part in a hundred thousand is obtained

The calculation of the dynamometer constants is summarised in Section V and the numerical work indicated

In the next section a description of the bifilar suspensions is given and an account of the determination of their directive force   The development of a method leading to greatly increased accuracy in the use of bifilar suspensions is presented partly in this and partly in the following section, and it is considered that this part of the investigation has been carried out with an accuracy considerably greater than one part in a hundred thousand

In Section VII a full account will be found of the deflection observations obtained when making the final measurements   The mean value involves 290 deflection readings, and the following figures show how closely the mean for certain definite sets of deflections can be repeated.   The figures are obtained with a complete readjustment of the circuit and general conditions in each case

84 656 cm	84 657 cm
84·655 „	84·657 „
84 656 „	84·656 „

In this section details are also given of the optical arrangements, the electrical connections and the application of certain impoitant corrections

The standard resistances are described in Section VIII   Their value was checked by a comparison with the standards in the Bureau of Standards at Washington.

Section IX deals with the ratio of the currents in the two systems of coils during deflection observations.   This ratio was measured by means of a Kelvin-Varley slide which had been specially calibrated for refined measurements   Thermal and contact effects were eliminated and the required accuracy was easily assured

The standard cells are discussed in Section X.   Comparisons weie made with cells at the Bureau of Standards at Washington in 1908 and 1909, and with those at the National Physical Laboratory at Teddington in 1909 and 1912   It has therefore been possible to express the mean of our cells in terms of the inteinational mean for the Weston normal cell

Insulation and magnetic tests are outlined in Section XI, and the final value for the electromotive foice of the international mean Weston normal cell is given in Section XII   This is found to be

1 01831 semi-absolute volts at 20° C

Some notes on the calibration and use of the Kelvin-Varley slide for very refined measurements are given in an appendix

On the Mercury Green Line λ = 5461 *Resolved by Glass and Quartz Lummer Plates and on its Zeeman Constituents*

By J C McLennan and A R McLeod, University of Toronto

[Plates 3 and 4]

Numerous investigators have studied the structure of some of the finer lines in the mercury arc, and other spectra, with ruled gratings, échelon spectroscopes, and Lummer plates, but up to the present when Lummer plates and échelons were used these were invariably made of glass   A short time ago a Lummer plate of crystal quartz was made for the Physical Laboratory at Toronto by the Adam Hilger Company, for the investigation of the structure of some of the finer lines in ultra-violet spectra, but before proceeding to use it for this purpose some measurements were made with it, and with two Lummer plates made of glass, on the wave-lengths of the satellites of the mercury green line λ = 5461 Å U   At the same time a precise method of measuring up the photographic fringe patterns produced by Lummer plates has been developed in which the geometrically central line of the double fringe pattern is taken as the line of reference in the measurements   This exact formula permits of the use of the fringes that emerge from the plate at nearly grazing direction, for which the dispersion is the greatest.   The following paper contains an account of the investigation and includes the values of the wave-lengths of the satellites of the green line as deduced by the application of the method to which reference has just been made   The quartz Lummer plate, it may be added, was cut with the axis of the crystal parallel to the plane refracting surfaces and perpendicular to the length of the plate

The source of the light used in the investigation was one or other of a number of ordinary Cooper-Hewitt mercury-arc lamps.   The light was passed through the collimator tube of a spectroscope and then into the plate in the usual manner

In studying the structure of the line the Lummer plates were always placed with their plane parallel faces vertical so that the light which issued from both plane faces was available for the production of the fringe pattern The light as it issued from the plate was allowed to fall upon the lens of a camera placed behind the Lummer plate, with the central plane of the lens perpendicular to the Lummer plate and its principal axis directed

along the central plane of the latter   By this arrangement the beams of parallel rays which issued at grazing emergence from both sides of the plate were brought to a focus in the line in which the central plane of the Lummer plate cut the focal plane of the lens while beams which issued in directions inclined at an angle to the plate were brought to a focus in the focal plane either to the right or to the left of the central line according as they issued from one side or the other of the Lummer plate

Photographs taken in this way of the fringe pattern produced by the Lummer plates with the light of the mercury green line include a set of wide main line fringes, and a number of sets of narrow fringes corresponding to the different satellites which accompany the main line

It is easy to show from the theory of Lummer plates that the fringes constituting any one of those sets are spaced out according to a very simple law   If, for example, we consider the main line set and take d to be the thickness of the Lummer plate, μ its refractive index for the wave-length λ, and b the focal length of the camera lens, and denote by $2\alpha_1, 2\alpha_J,$ $, 2\alpha_n,$ the distances between the centres of the main line fringes taken in pairs, one being on either side of the central line of the photograph, then it can be shown that

$$\lambda = \frac{d}{b^2} \cdot \frac{\alpha_n^2 - \alpha_{n-1}^2}{\sqrt{(\mu^2 - 1)}}, \tag{1}$$

so that the quantity $\alpha_n^2 - \alpha_{n-1}^2$ should to a very close degree have the same value over the whole fringe pattern, i e denoting $\alpha_{n+m}^2 - \alpha_n^2$ by Ω_m, and $\alpha_n^2 - \alpha_{n-1}^2$ by Ω_1, we should have for the whole pattern

$$\Omega_m / m = \Omega_1 = \text{a constant} \tag{2}$$

For let the two systems of emergent parallel rays which go to form bright fringes of the nth and $(n+m)$th orders issue from the plate at the angles ψ and ψ' respectively   Then, denoting the path differences corresponding to these two fringes by γ and $\gamma + m\lambda$, we have

$$\gamma = 2d\sqrt{(\mu^2 - \cos^2 \psi)}, \quad \text{and} \quad \gamma + m\lambda = 2d\sqrt{(\mu^2 - \cos^2 \psi')}$$

From these two equations we have

$$m\lambda = 2d \frac{\cos^2 \psi - \cos^2 \psi'}{\sqrt{(\mu^2 - \cos^2 \psi')} + \sqrt{(\mu^2 - \cos^2 \psi)}},$$

or, if the angles ψ and ψ' are small,

$$m\lambda = \frac{d}{b^2} \frac{\alpha_{n+m}^2 - \alpha_n^2}{\sqrt{(\mu^2 - 1)}}$$

Numerous tests were made of the law given by equation (2) by measuring up a number of photographs of the fringe patterns obtained with the different Lummer plates, and it was found to hold invariably with very

great exactness   One particular case in which it was possible to measure the distances between the bands corresponding to 11 different orders on the plate may be cited   The values of a_1, a_2,   , a_n, and a_1^2, a_2^2,   . a_n^2 for this plate are given in Table I, from which it will be seen that the latter are in arithmetical progression, so that the values of Ω_1 deduced from $\Omega_1 = \Omega_m/m$ are in close agreement, and the most probable value of Ω_1 can be deduced by well-known methods.   The uniformity exhibited in the values of Ω_1 shows decisively that the law enunciated above represents exceedingly closely the distribution of the fringes in the Lummer plate pattern

Table I —Determination of Ω_1 from 11 Orders of Main Line Fringes
obtained with a glass Lummer plate, by means of Equation (2)

	Difference		Difference
$\alpha_1 = 0\,5697$		$\alpha_1^2 = 0\,3246$	
$\alpha_2 = 0\,8428$	0 2731	$\alpha_2^2 = 0\,7103$	0 3857
$\alpha_3 = 1\,0478$	0 2050	$\alpha_3^2 = 1\,0979$	0 3876
$\alpha_4 = 1\,2194$	0 1716	$\alpha_4^2 = 1\,4870$	0 3891
$\alpha_5 = 1\,3677$	0 1483	$\alpha_5^2 = 1\,8706$	0 3836
$\alpha_6 = 1\,5022$	0 1345	$\alpha_6^2 = 2\,2566$	0 3860
$\alpha_7 = 1\,6264$	0 1242	$\alpha_7^2 = 2\,6452$	0 3886
$\alpha_8 = 1\,7407$	0 1143	$\alpha_8^2 = 3\,0300$	0 3848
$\alpha_9 = 1\,8488$	0 1081	$\alpha_9^2 = 3\,4181$	0 3881
$\alpha_{10} = 1\,9499$	0 1011	$\alpha_{10}^2 = 3\,8021$	0 3840
$\alpha_{11} = 2\,0460$	0 0961	$\alpha_{11}^2 = 4\,1862$	0 3839

In this connection it may be pointed out that for lines whose wavelengths are so close together as those of the main component and those of the satellites of the mercury green line the value of Ω_1 should come out about the same, when deduced either from measurements on the fringes of the main line system or from those made on the fringes of a satellite system   That this is true may be seen from the values of Ω_1 given in Table II, which were deduced from measurements similar to those described above made upon the same plate on the fringe system of positive satellite 0 093, of positive satellite 0 138, of negative satellite 0·07, as well as on the system of fringes due to the main component.

Table II

Fringe pattern of	Deduced value of Ω_1
Satellite 0 138	0 3860
Satellite 0 093	0 3862
Main component	0 3863
Satellite −0 07	0 3856

The formula referred to above as the one used by us in determining the differences between the wave-lengths of the different satellites, and the wave-length of the main constituent of the green line, is expressible in the form

$$\Delta\lambda = \frac{\delta(\alpha^2)}{\Omega_1}\Delta\lambda_m, \tag{3}$$

where Ω_1 has the significance given to it above, and is equal to the difference between the squares of the distances of two consecutive main line fringes from the central line of the fringe pattern, i.e., $\alpha_{m_1}^2 - \alpha_m^2$ and $\delta(\alpha^2)$ denotes either the expression $\alpha_{m_1}^2 - \alpha_s^2$ or $\alpha_s^2 - \alpha_m^2$, where α_m is the distance of a main line fringe from the central line of the pattern, α_{m_1} that of the main line fringe of the next higher order, and α_s is the distance from the central line of a satellite fringe of the same order as α_m. $\Delta\lambda_m$ represents that change in the wave-length of the light which would cause the fringe of the mth order of the system of fringes due to light of wave-length $\lambda + \Delta\lambda_m$ to coincide with the fringe of the $(m+1)$th order of the system formed by the light of wave-length λ.

The value of $\Delta\lambda_m$, as v Baeyer[*] has shown, is given by

$$\Delta\lambda_m = \frac{\lambda^2 q}{q^2\lambda - 4d^2\mu\,d\mu/d\lambda}, \tag{4}$$

where

$$q = \frac{2d}{\lambda}\sqrt{(\mu^2 - 1)} \tag{5}$$

and is calculable for any wave-length λ when the thickness of the Lummer plate, and its refractive index as well as its dispersion for the wave-length λ, are known.

The validity of the equation $\Delta\lambda = \frac{\delta(\alpha^2)}{\Omega_1}\Delta\lambda_m$ can be seen by throwing it into the form

$$\alpha_s^2 = \frac{\Omega_1}{\Delta\lambda_m}\Delta\lambda + \alpha_m^2, \tag{6}$$

where α_s and $\Delta\lambda$ are taken to be the variables

In this form the relation shows that in the interference point-pattern formed by crossing a Lummer plate with an échelon grating, the points corresponding to the different satellites of any selected order all lie on one parabola The beautiful diagrams accompanying the paper by Nagaoka and Takamine[†] amply illustrate this point

In using the formula $\Delta\lambda = \frac{\delta(\alpha^2)}{\Omega_1}\Delta\lambda_m$ for determining the wave-length

    * v Baeyer, 'Verh d Deutsch. Phys. Ges.,' p. 734, No. 18/20, 1908
    † Nagaoka and Takamine, 'Phys. Soc. Lond Proc.,' vol 25, pt. 1, Dec. 15, 1912.

differences Δλ for the different satellites of a main line the quantities to be determined by measurement are Ω_1, viz, $\alpha_{m_1}^2 - \alpha_m^2$, and $\delta(\alpha^3)$, i e, $\alpha_s^2 - \alpha_m^2$ As we have pointed out above, Ω_1 is found by measuring the distance between pairs of corresponding main line or satellite fringes, one member of each pair being on either side of the double pattern   Similar measurements made on pairs of any selected satellite's fringes will give the values of α_s^2 for the different orders for this satellite   The quantity $\alpha_s^2 - \alpha_m^2$ can then be found Since this quantity, as equation (3) shows, should have the same value for all orders, the mean of its values taken over all the orders in the fringe pattern should give a very accurate result

In the present investigation the formula $\Delta\lambda = [\delta(\alpha^3)/\Omega_1]\Delta\lambda_m$ was used in deducing Δλ for the different satellites of the mercury green line from measurements on eight different photographs taken with the quartz plate, and all the results are recorded in Table III, wave-lengths being given in Ångström units   The values obtained from the different photographs are all in good agreement   It will be seen that the fringes due to the negative satellite No 5 found by one of us* with an échelon grating and by a number

Table III.

Data for quartz Lummer plates	Refractive indices	
	λ	μ
$d = 0\ 47$ cm	7065 59	1 54949
$\lambda = 5461 \times 10^{-8}$ cm	6563 04	1 55095
$\mu = 1\ 55537$	5893 17	1 55337
$d\mu/d\lambda = -528°$	5607 1	1 55462
$\Delta\lambda_m = 0\ 2582$ Å U	5270 11	1 55639
	4861 49	1 55899

Plate	Negative satellites			Positive satellites		
	No 5	No 4	No 3	No 1	No 2	No 3
No 1		−0 108	−0 075	0 079	0 1195	0 206
„ 2		−0 108	−0 075	0 0795	0 1203	0 206
„ 3		−0 107	−0 074	0 0795	0 1204	0 207
„ 4		−0 110	−0 078	0 0794	0 1184	0 204
„ 5		−0 108	−0 073	0 0817	0 1185	0 207
„ 6		−0 107	−0 077	0 0781	0 1216	0 205
„ 7		−0 107	−0 075	0 0789	0 1198	0 206
„ 8		−0 104	−0 074	0 0788	0 1230	0 207
Mean		−0 107	−0 075	0 0794	0 1202	0 206

* McLennan, 'Roy Soc. Proc.,' A, vol. 87, p. 269 (1913).

of other experimenters at about $-0\,243$ Å U did not appear on the photographs taken with the quartz plate ' This was because the fringe for this satellite of any order always coincided in the pattern with the main line fringe of the next lower order

A similar uniformity marked the results obtained from measurements made on a great many photographs taken with the glass Lummer plates Illustrations of these are given in Table IV, which contains the values of $\Delta\lambda$ in A U. for the different satellites found from two photographs taken with one of the glass plates, and from one taken with the other No values are given for the $\Delta\lambda$ of positive satellite No 3, situated at about $0\,210$ A U , as the fringes for it did not appear on any of the photographs, owing very probably to their overlapping or lying very close to those of negative satellite No 3

Table IV

Data for glass Lummer plates	Refractive indices	
	λ	μ
$d = 0\,448$ cm	$6563\,045$	$1\,50746$
$\lambda = 5461 \times 10^{-3}$ cm	$5896\,155$	$1\,50990$
$\mu = 1\,5121$	$5890\,186$	
$d\mu/d\lambda = -530$	$4861\,49$	$1\,51560$
$\Delta\lambda_m = 0\,2984$ Å U	$4308\,08$	$1\,52025$

	Negative satellites			Positive satellites		
	No 5	No 4	No 3	No 1	No 2	No 3
Lummer Plate A— Pattern No 1	$-0\,245$	$-0\,108$	$-0\,069$	$0\,092$	$0\,137$	
„ „ 2	$-0\,246$	$-0\,109$	$-0\,071$	$0\,092$	$0\,137$	
Lummer Plate B— Pattern No 1	$-0\,244$	$-0\,108$	$-0\,069$	$0\,094$	$0\,139$	
Mean	$-0\,245$	$-0\,108$	$-0\,070$	$0\,093$	$0\,138$	

The mean values of $\Delta\lambda$ for the different satellites of the mercury green line deduced from those in Tables III and IV are collected in Table V, and along with them are also given a number of determinations of the $\Delta\lambda$ for the satellites of the line found by other investigators with different types of resolving apparatus. From this table it will be seen that Nagaoka and Takamine were able to resolve the main line into a doublet with $-0\,026$ as the position of the constituent of shorter wave-length As the table shows, the main line was not resolved into a doublet either by the quartz

plate or by the glass plates used by us   Nagaoka and Takamine also give a faint satellite at about $-0\,054$ This satellite, it will be noted, was not distinguishable on any of our photographs, either in the work with the Lummer plates or in that done by one of us with an échelon   Moreover, it does not appear among the list of satellites for the line given by Gale and Lemon in the report of their investigation of the structure of the line with a Michelson grating   From the character of Nagaoka and Takamine's work, however, it would appear that this satellite has a real existence

Table V —Values of $\Delta\lambda$ for Satellites of Mercury Green Line $\lambda = 5461$ A U

Resolution by	Negative satellites					Main line	Positive satellites		
	No 5	No 4	No 3	No 2	No 1		No 1	No 2	No 3
McLennan and McLeod—									
Glass Lummer plates	$-0\,245$	$-0\,108$	$-0\,070$			0	$0\,093$	$0\,138$	
Quartz Lummer plate		$-0\,107$	$-0\,075$			0	$0\,079$	$0\,120$	$0\,206$
McLennan*—									
Echelon	$-0\,243$	$-0\,104$	$-0\,070$			0	$0\,090$	$0\,135$	$0\,210$
Gale and Lemon†—									
Michelson grating	$-0\,246$	$-0\,107$	$-0\,067$			0	$0\,070$	$0\,117$	$0\,204$
Nagaoka and Takamine‡—									
Echelon	$-0\,246$	$-0\,113$	$-0\,080$	$-0\,055$	$-0\,026$	0	$0\,072$	$0\,118$	$0\,204$
Echelon crossed with Lummer plate	$-0\,242$	$-0\,108$	$-0\,074$	$-0\,054$	$-0\,026$	0	$0\,078$	$0\,123$	$0\,210$

* McLennan, 'Roy. Soc Proc,' A, vol 87, p 269 (1912)

† Gale and Lemon, 'Ast Phys Journ,' January, 1910, 'Phys Zeit,' vol 11, p 209 (1910)

‡ Nagaoka and Takamine, 'Phys Soc Proc,' London, p 1, December 15, 1912

The positions of the negative satellites Nos. 3, 4, and 5, as found by the various types of apparatus, it will be seen from the table are all in good agreement   A discrepancy exists, however, in regard to the positions of the positive satellites Nos 1 and 2   The glass Lummer plates used by the writers, and the échelon resolution obtained by one of us, give these satellites at about $0\,092$ and $0\,137$, while the resolutions by Gale and Lemon, by Nagaoka and Takamine, and by the writers with the quartz Lummer plate, give the positions of these two satellites at about $0\,079$ and $0\,120$ In order, if possible, to remove this discrepancy a number of photographs of the fringe patterns formed both by the quartz Lummer plate and by the two glass ones were taken with the light from Cooper-Hewitt lamps of diameters ranging from 1 to $2\frac{1}{2}$ cm run with current intensities of from 4 to 7 ampères, but the positions of these two satellites always came out, when the plates

were measured up, in close agreement with the numbers given in Tables III and IV

In one particular case a photograph of the fringe pattern formed by the quartz Lummer plate was taken simultaneously with the one formed by one of the glass Lummer plates, when the collimators of the spectroscopes carrying those two plates were directed at the same portion of the arc in the Cooper-Hewitt lamp   The values of $\Delta\lambda$ found for positive satellites Nos. 1 and 2 from the pattern formed by the glass plates were respectively 0 093 and 0 137 while the values found from the photograph taken with the quartz Lummer plate were 0 081 and 0 124   This result would go to show that the discrepancy did not arise from any real variation in the structure of the line It will be seen, moreover, that while the resolution by the glass plate gave the wave-length of positive satellite No 2 as 0 044 longer than that of positive satellite No 1, that by the quartz plate gave it as 0 043 longer, which is practically the same   This might seem to indicate that the discrepancy arose from an error in setting the micrometer on the main line fringes in measuring up the plates   Such an error, however, should affect the values of $\Delta\lambda$ for all the satellites in a similar way and should not introduce any error in the determination of the wave-lengths of the positive satellites 1 and 2 relative to those of any of the other satellites   The results in Table V show, however, that while the values of $\Delta\lambda$ for these two satellites relative to each other are the same, for both the glass and quartz plates, their values relative to those of negative satellites Nos 1 and 2, for example, are considerably different for the two kinds of plates

It may be pointed out that all the photographs from which the values of $\Delta\lambda$ given in Table III were obtained were taken with light emitted by the plate which belonged to the extraordinary ray system   A few photographs were also taken of fringe patterns formed by the ordinary ray system and these were all found to give values for $\Delta\lambda$ for the different satellites practically the same as those given in Table III.   In one particular instance a photograph was taken of the pattern formed by the extraordinary rays and immediately afterwards one formed by the ordinary system   When these two plates were measured up to find $\Delta\lambda$ for positive satellite No 1 its value came out from the ordinary ray pattern as 0 078 and from the extraordinary ray pattern as 0 080   From these considerations it will be seen that the explanation of the discrepancy is by no means evident.   All the measurements were made with extreme care and the calculations were always carefully checked over   As pointed out in Table III, the value of $\Delta\lambda_m$ was calculated to be 0·2582 for the fringe system formed by the extraordinary rays.   For the ordinary ray system of fringes its value was 0·2608.   As these values differ by only 1 per cent., it

is clear that if any error were made by inadvertently assuming a pattern to be formed by the extraordinary rays, for example, when it was really made by the ordinary ones, the value found for $\Delta\lambda$ would still be correct to within one unit in the third decimal place. It is interesting to note that the values of $\Delta\lambda$ for the satellites found by us with the quartz plate are extremely close to those found by Nagaoka and Takamine with a glass plate, when the system of measurement used by them was presumably different from the one used by us

Relations between the Positions of the Satellites

In dealing with the origin of satellites Hull[*] has pointed out that a periodicity exists in the spacing of the satellites of some of the mercury lines, which one is scarcely warranted in considering to be accidental. Nagaoka[†] in an earlier communication had also referred to this matter and in his later paper in conjunction with Takamine (*loc. cit.*) he has again dealt with the subject. Although it has been shown that the values of $\Delta\lambda$ for some of the satellites of the mercury lines 5461, 4078 and 4047 are in a simple ratio, it does not appear to have been noted that with the negative satellites of the line 5461 the $\Delta\lambda$ for any one satellite can be obtained by simply taking either three-halves or nine-fourths of the $\Delta\lambda$ for the satellite next closer than it to the main line

This may be seen from the results collected in Table VI

With the positive satellites of the line 5461 Å U, the 3 : 2 ratio also applies, as Table VI shows, to the values of $\Delta\lambda$ found for these satellites by the writers with the glass Lummer plates, and by one of us with an échelon grating, but for the values of $\Delta\lambda$ for the positive satellites found by Nagaoka and Takamine and also by the writers with the quartz Lummer plate, it will be seen that while the values of the $\Delta\lambda$ for satellites Nos. 1 and 2 are in the ratio 2 : 3, the values of $\Delta\lambda$ for satellites Nos 2 and 3 are more nearly in the ratio 3 : 5

The suggestion of the existence of such a law as that mentioned regulating the distribution of the satellites, brings with it the notion that possibly the main constituent of the green line itself might be shown with suitable conditions and apparatus to consist of a great number of very close lines. Some experiments recently made by Janicki,[‡] moreover, afford some grounds for this idea. In these the source of the light was an Arons-Lummer mercury lamp, which was kept very cold and was driven with a direct current of 2·5 ampères. The circuit also had included in it a coil of high self-induction.

* Hull, 'Astrophys. Journ.,' vol. 32, p 226 (1910).
† Nagaoka, 'Phys. Zeit,' vol 10, p. 609 (1909).
‡ Janicki, 'Ann. der Phys.,' vol. 39, p. 439 (1912).

Table VI —Satellites of Mercury Line λ = 5461 Å U

Satellites		Calculated	Observed	
			Nagaoka and Takamine	McLennan and McLeod
		Ratio 3 2		Glass and quartz plates
Negative No	5	—0 245	—0 242	—0 245
		—0 163		
„ „	4	—0 109	—0 108	—0 108
				—0 107
, „	3	—0 073	—0 074	—0 070
				—0 075
, „	2	—0 048	—0 054	
		—0 036		
„ „	1	—0 024	—0 026	
Positive No	3	0 210		Glass plate
„ „	2	0 140		0 138
„ „	1	0 093		0 093
		Ratio		Quartz plate
Positive No	3	0 210 5 3	0 210	0 206
„ „	2	0 126 3 2	0 123	0 120
„ „	1	0 084	0 078	0 079

When the light from this lamp was examined with a system consisting of a Lummer-Gehrcke plate 0 971 cm. thick and 30 cm long, crossed with a wedge-shaped plate 0 628 cm thick possessing a wedge angle of 40″, Janicki found that the main component of the green line consisted of a series of five well-marked, very close lines Thus the suggestion is open that the green line consists of a series of lines closing together towards the centre, their positions being regulated by some law which in the outer components simplifies approximately to the geometric progression exhibited in Table VI

It is interesting to note that a similar law having the ratio 3 5 as a basis, approximately holds in regard to the distribution of the satellites of the mercury line λ = 3341. This line belongs to the same series as the line λ = 5461, and is next in order to it But little attention has been given as yet to the structure of this line except by G Wendt,* who examined it with a Rowland grating, and reports it as consisting of a strong main component accompanied by four satellites of wave-length greater and by four of wave-length shorter than the main component These are all collected in Table VII, and it will be seen that while the departures from the law are more marked than in the case of the line λ = 5461, there is a fairly

* Wendt, 'Ann der Phys,' Folge IV, No. 37, p. 535 (1913).

good agreement between the observed values of Δλ and those calculated on the basis of the 3/5 law

Table VII —Satellites of the Mercury Line λ = 3341 Å U

Satellites	Values of Δλ calculated on basis of ratio 5 3	Values of Δλ observed by Wendt
Negative satellites—		
No 4	−0 600	−0 592
„ 3	−0 360	−0 357
„ 2	−0 216	−0 198
„ 1	−0 180	−0 101
Positive satellites—		
No 4	0 500	0 497
„ 3	0 300	0 299
„ 2	0 180	0 181
„ 1	0 108	0 127

The Zeeman Effect

In the course of the investigation into the structure of the green line λ = 5461 with the Lummer plates, it was noticed that these plates provided an excellent means of illustrating the Zeeman effect with this line and of determining from it the ratio e/m by a method of coincidence

In making the observations the Cooper-Hewitt lamp was placed longitudinally in the field of an electromagnet provided with pierced pole-pieces The mechanical details of the manner in which this was done have already been described in a previous communication by one of us *

The light emitted by the lamp in a direction at right angles to the field was passed through a collimator and into the Lummer plate in the usual way On emerging from the Lummer plate, the light was then passed through a Wollaston double-image prism and afterwards allowed to fall upon the lens of the camera   With this arrangement the image in the focal plane consisted of two patterns of fringes which overlapped over a portion of their length   Care was taken to give the Wollaston prism such an orientation that with no field the fringes in the upper pattern were directly in line with those in the lower   It was also arranged that the light forming the upper pattern was polarised by the prism in a plane perpendicular to the lines of force, and that forming the lower pattern polarised in a plane parallel to the field

On passing a current of small intensity through the electromagnet the main line fringes in the upper pattern became somewhat widened but were not displaced as a whole   On the other hand, each of the main line fringes

* McLennan, 'Roy Soc. Proc,' A, vol. 87, p 273 (1912).

in the lower pattern became slightly widened and split up into a doublet, one member of the doublet being displaced to the right and the other to the left of the position initially occupied by the fringe

When the field of the electromagnet was gradually increased, the fringes in the upper pattern continued to widen and finally broke up into well-marked triplets. On the other hand, the members of the doublet in the lower pattern continued to separate from each other and to widen, and each finally broke up into a triplet. In this way it was readily shown that the green line broke up into a nonet under moderate fields with the components of the outer triplets polarised parallel to the lines of force and the components of the inner triplet polarised perpendicularly to the lines of force. The method just described also brought out the point that all the members of the nonet were of equal intensity and that they were regularly and equally spaced

The method of coincidence which was applied consisted in so choosing the magnetic field, that the outer triplet on the left-hand side of one order in the lower pattern exactly overlapped and coincided with the outer triplet on the right-hand side of the next higher order of the same pattern. When fields stronger than those required for coincidence were used, the outer triplets in the lower pattern moved beyond the position of coincidence and produced a confused and indecipherable effect. In the upper pattern the effect of increasing the field was only to spread out and make more marked the members of the triplet

It is easy to see that when coincidence takes place the change in wavelength, $\Delta\lambda$, of each of the central members of the outer triplets of the nonet relative to that of the undisplaced line is equal to $\frac{1}{2}\Delta\lambda_m$

For coincidence we have then e/m given by $\frac{e}{m} = \frac{2\pi C \Delta\lambda_m}{H\lambda^2}$ In making a test of this method in which no special care was taken to get a highly accurate result it was found that coincidence was obtained with a field of 6921 gauss. Since for the Lummer plate used $\Delta\lambda_m$ was equal to $0\cdot2984 \times 10^{-8}$ cm, it followed that $e/m = 2\cdot73 \times 10^7$ From this we have for a normal triplet $e/m = 1\cdot82 \times 10^7$, a value which is close to that found in some of the best determinations[*] with the lines in the mercury arc spectrum

<div align="center">Summary.</div>

1 The formula $\Delta\lambda = \frac{a_b{}^2 - a_m{}^2}{a_{m_1}{}^2 - a_m{}^2}\Delta\lambda_m$ has been shown to be the one which

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[*] Nagaoka, 'Nature,' May 5, 1910, p. 377.
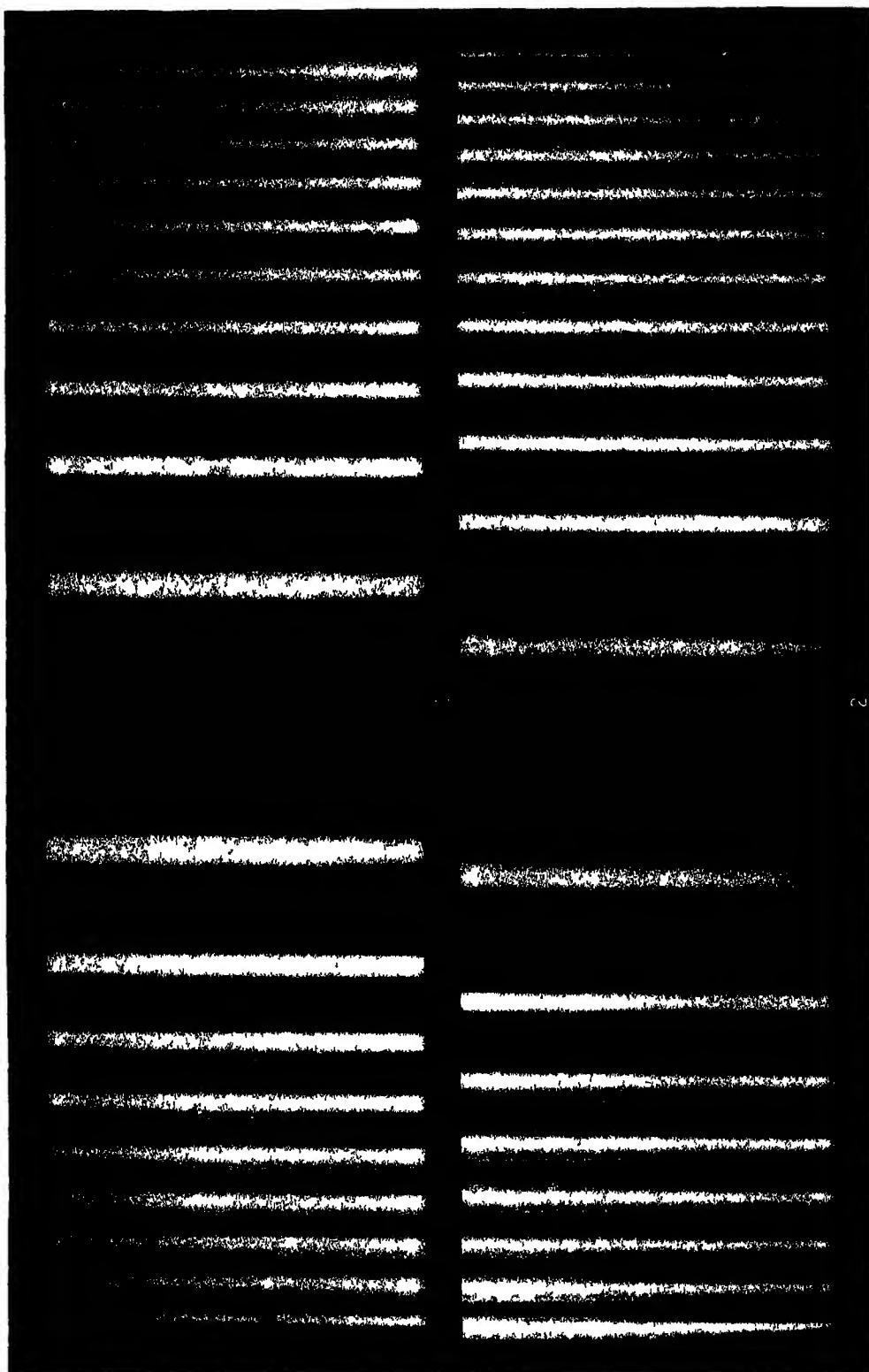
should be used in measuring up the fringe pattern produced by Lummer plates for determining small changes in wave-length.

2. This formula has been applied to the determination of the positions of the satellites of the mercury line λ = 5461 Å.U relative to the main component, when the line was resolved by a Lummer plate made of crystal quartz and also by two others made of glass. The results obtained with the quartz plate agree with the values recently found by Nagaoka and Takamine, who used a glass Lummer plate crossed with an échelon grating, while those obtained with the glass Lummer plates agree best with determinations previously made by one of the writers with an échelon grating.

3. Considerations have been presented in favour of the view that the green line consists of a series of lines closing together towards the centre, their position being regulated by some law which in the outer components simplifies approximately to a geometric progression. Evidence is also adduced in support of the view that a somewhat similar law applies approximately to the mercury arc line λ = 3341 Å U

4. A method of coincidence was used to illustrate the magnetic resolution of the mercury green line λ = 5461 Å.U. and a value of 1 82 × 10⁷ has been obtained for *e/m*.

In conclusion the writers wish to convey their thanks to Mr. P. Blackman and Mr D. A. Keys for assistance in taking the photographs and in checking up the measurements of some of the plates.

DESCRIPTION OF PLATES.

Fig 1 illustrates the fringe pattern obtained with the quartz Lummer plate. Proceeding outwards from the central portion of the pattern either to the right or to the left, the significance of the fringes between any two orders of main line fringes is as follows: Main line, positive satellite No. 1, positive No. 2, negative No. 4, negative No 3, positive No. 3, and main line

In fig 2 the pattern obtained with one of the glass Lummer plates is reproduced. The order of the fringes in this pattern, proceeding outwards, is as follows :—Main line, negative satellite No 5, positive No 1, positive No. 2, negative No. 4, negative No. 3, and main line.

Fig. 3 illustrates the magnetic resolution of the green line λ = 5461 Å.U under the conditions described The line is broken up into a nonet, and the members of the outer triplets of any order are in coincidence with the members of the outer triplets of the next adjacent order.

On the Electrification Produced during the Raising of a Cloud of Dust

By W A Douglas Rudge, M A

In a paper published in the 'Philosophical Magazine' of May, 1913, an account is given of some experiments which show that the raising of a cloud of dust is accompanied by the production of a large amount of electricity The dust was usually blown away from the surface of a flat piece of material or from the end of a tube.   Large quantities of electricity were produced by this means and the sign of the charge seemed to depend upon the nature of the material used to form the dust cloud   Basic bodies generally acquired a negative charge, and acidic bodies a positive charge It might be suggested that the origin of the charges lay in the friction of the particles of material against the surface from which they were blown, but this, however, is not altogether the case, as the following experiment will show

An insulated brass tube, 25 cm in length and 1 5 cm in diameter, was connected to an electroscope   Tubes of different materials and of a slightly smaller diameter were provided to fit inside it so that the nature of the surface from which the dust was blown could be varied.   Under these circumstances it might be expected that the charge carried away by the dust, and also that retained by the tube, would vary with the nature of the surface, but this was not the case, for with the same substance for creating the dust, the electrification was always the same no matter what was the nature of the surface from which it was blown.   For example, sand always furnished a positive charge and red lead a negative one, and other materials gave charges of the signs given in the paper referred to   Again, the nature of the surface against which the dust was projected was also without influence upon the charge acquired.   Clouds of dust were raised by blowing a current of air through the dust contained in a small wash-bottle, and the cloud projected against an insulated plate connected to an electroscope.   The charge gained by the plate was of the same sign whether the plate was rough or smooth, or coated with different materials, so that it appears evident that the charge is actually produced upon the dust cloud itself   It has been shown that the charge upon the dust is apparently[*] accompanied by one of opposite sign upon the air, and a convenient arrangement for showing the presence of these two charges is

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[*] See note, p. 263.

given in fig. 1   The dust raised by blowing air through W is projected against the wire gauze screen G and the greater portion is caught, but the air
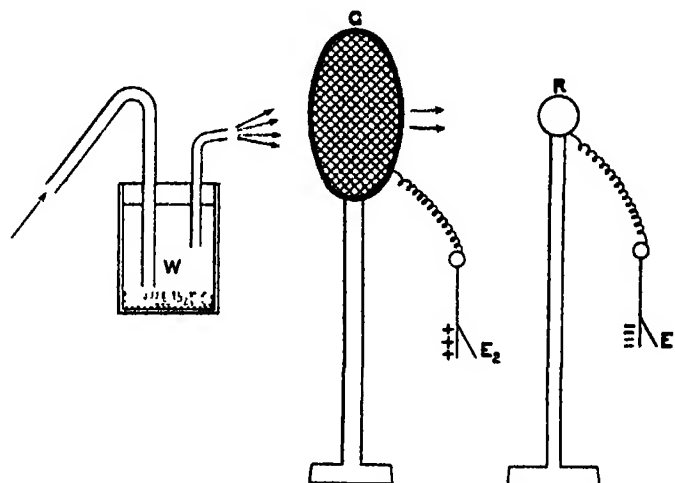
FIG. 1.

accompanying the dust is carried on   At some distance (50–100 cm) behind the gauze a small radium-coated plate R served to collect any charge present upon the air.   Electroscopes E_2 and E_1 indicate the charges acquired by G and R   A few typical cases are given in Table I

Table I

Dust	Charge upon gauze	Charge upon air
Red lead	−	+
Sand	+	−
Flour	−	+
Mercuric sulphide	+	−
Arsenious oxide	+	−
Zinc dust	−	+
Iron filings	−	+
Chalk	−	+

The electrification indicated by E_1 is not due to the friction of the dust against the wire gauze, for a charge of the same kind is shown by spraying the dust directly into the air

Up to this point the work had been carried on at the University College, Bloemfontein, and in the open air, but since then the experiments as detailed in the original paper have been repeated under different climatic conditions, and also within a room in the Cavendish Laboratory.   The result has

been to confirm the previous experiments, and although some variations do occur, the general laws appear to be well substantiated

In the earlier experiments there was a more or less free motion of air and dust permitted, but it was thought advisable to conduct the experiment in a confined space   For this purpose a wooden box 45 × 45 × 55 cm was lined with tinfoil, and dust clouds raised in this by spraying through a hole in the side   Insulated conductors could be arranged inside, either to take the charge upon the dust, or upon the air   Wires connected to the electroscopes were passed through thick ebonite plugs into the box, one wire being attached to an insulated cylinder V just close to the hole through which the dust was projected, and the other to a small radium-coated plate R which was not in the direct path of the dust from the hole, fig 2   With this
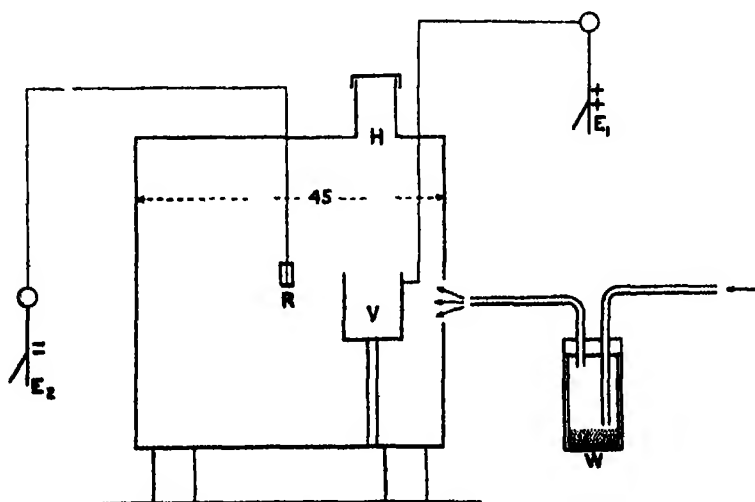
Fig 2

Table II.—Showing Charges on Air and Dust.

Substance	Charge on air	Charge on dust.
Red lead	+	—
Mercury sulphide	—	+
Silica	—	+
Chalk	+	—
Zinc	+	—
Sulphur	—	+
Flour	+	—
Morphine	+	—
Amygdalin	—	+
Quinine	+	—
Quinine sulphate	—	+

apparatus a number of experiments were made which showed practically the same results as those obtained by spraying in the open air   If the material used was silica, the charge upon the insulated vessel was positive and the charge upon the air negative, as would have been the case in the open air   If red lead was used, the charges upon conductor and air were negative and positive respectively

This arrangement was very sensitive as a means of detecting the charge upon the air, and some attempts were made to get quantitative results, that is to find some relation between the charge of electricity upon the air and the quantity of material sprayed.   Mercury sulphide was the substance used, as this was found to be the most efficient dust for producing electrification, but the efficiency depended upon the fineness of the powder   The finely powdered material was contained in a small wash-bottle, and the dust cloud raised by blowing air from a small rubber spraying bellows through it   It was found that fairly constant amounts of dust were carried away in each puff of air from the rubber spraying ball, but the amount was so small that it was practically unweighable, and the weight of the material associated with one puff had to be found as a mean from a considerable number of puffs   In this case a Dolezalek electrometer was used instead of an electroscope, as of course it was more sensitive   On sending the dust cloud into the box it was found that one puff was sufficient to charge the radium collector up to a potential of from 6 to 8 volts

In order to find the average weight of material the wash-bottle was weighed carefully and then a definite number of puffs made and the bottle weighed again   If the material had been well sifted before being put in the bottle this gave very concordant results, as the table shows

Table III —Weight of Bottle and Contents.

		Loss in weight for 10 puffs
Before puffing	78 177 grm.	
After 10 puffs	78 172	0 ·005 grm.
„ 20 „	78 1678	0 ·0047
„ 80 „	78 1625	0 ·0048
„ 40 „	78 ·158	0 ·0045
„ 60 „	78 1686	0 ·0044
„ 70 „	78 144	0 ·0096 (20 puffs)

Loss for 70 puffs .   . .   . 0·033   grm.
„   1 puff   .   . . 0 00047   „

The mean of six series of similar determinations gave an average of 0·00053 grm. of HgS per puff

Practically the whole of the volume of the air inside the box was charged, and assuming for a moment that the material was uniformly distributed throughout the volume of the air the amount of dust per cubic centimetre would be

$$\frac{0\ 00053}{45 \times 45 \times 55} = 5 \times 10^{-9} \text{ grm. per c c. approximately for one puff}$$

Other material gave similar results, but nothing so far tested approaches mercury sulphide in the small amount required to produce a given charge Molybdic acid was also very efficient   This small amount of dust, 5×10^{-9} grm. per cubic centimetre, gave a charge which raises the potential of the exploring electrode to several volts, so that the actual amount of dust which would produce a detectable charge might well be $1/1000$ of this amount

Blowing a few centigrammes of cornflour into a large room* charged the air to such an extent that a radium-coated collector rapidly indicated a potential of 200 volts, and the charge persisted for some time

It is thus easy to understand how the very high potential gradient—over 10,000 volts per metre—may arise during a dust storm, and the lightning flashes which are stated to accompany eruptions of fine ashes from volcanoes may perhaps be referred to the same cause

On several occasions it had been noted that a reversed charge was given to the wire gauze used to collect the dust, and this appeared to be due to the rate at which the cloud of dust was raised, as well as to the influence of the opposite charge upon the air.   The box used for the last series of experiments was employed to carry out another series in which the dust was "rained" into the box instead of being sprayed.   A hole, H, was bored in the top of the box and immediately below this a hollow insulated copper vessel connected to a Dolezalek electrometer was arranged   A radium collector could also be inserted when desired (fig. 2).   The dust was sifted through fine lawn and in this case the curious result was obtained of a negative charge being nearly always given up to the insulated vessel, and the air as tested by a radium-coated conductor was also negative   Only very small amounts of material passed through the close meshes of the sieve , a milligramme or so of most substances would raise the potential of the insulated conductor to 3 or 4 volts   Varying the *distance of fall* from 10 to 30 cm. had *no* influence on the nature of the charge, but merely dropping the powder in a mass produced no charge, it being necessary apparently for the particles to be spread apart or rubbed together if a charge was to be obtained.   For example, some

* The room had a volume of about 250 cubic metres.

reduced iron was dropped down a glass tube 40 cm in length into the insulated vessel, and practically no charge was generated, but on tying a piece of fine lawn over the end of the tube and tapping, it gave a charge which sent the spot of light off the scale   Table IV gives some of the results

Table IV

Material	Charge, raining	Charge, spraying
Silica	Negative	Positive
Mercury sulphide	„	„
Red lead	Very slight negative, sometimes +	Negative
Precipitated sulphur	Negative, but not strong	Positive
Iron filings	„ „	Negative
Chalk	Very slight, but tending to −	„
Zinc dust	Negative*	„
Morphine	„	„
Cornflour	„	Positive
Ground crystallised sulphur	„	„

* Varied with height of fall, above 20 cm sometimes positive

The experiments described so far had been carried out with air, and it seemed of interest to repeat them with the gases which can be obtained in cylinders, the pressure under which these gases escape furnishing a convenient method of raising the dust   The gases available were oxygen, hydrogen, carbonic acid, sulphur dioxide, nitrogen, and ammonia.   Using the wash-bottle arrangement for raising the dust, a series of puffs of gas was sent through the bottle and the dust raised tested in the usual manner.   Generally the same charges as with air were obtained.

A considerable amount of time was expended in endeavouring to measure the current which could be sent through air when dust was present, but the results were very unsatisfactory on account of the large charges initially present upon the dust   If ions are present, they most probably are of a large size, and hence would have a small velocity in a field of moderate strength, and under any circumstances a certain number of charged dust particles would reach conductors connected to the electrometer, but the current through the dust-laden air was very small.   The general trend of the experiments seems to indicate that the air does become slightly ionised but not to an extent comparable with that produced by a trace of a radium preparation.

Up to the present no satisfactory explanation as to the origin of the charges had presented itself save the one that these charges might be due in some way to the enormous increase of surface of contact between the air and the dust which must occur when a small amount of powder is blown into a dust-

cloud, somewhat in the same manner as a strong charge is produced by breaking up a liquid into a fine spray as shown by Lénard and others, and some experiments were made to test whether this was the case

A brass tube, A, 30 cm in length and 1 5 cm in diameter, was provided with a wire gauze cap at G and projected into a copper vessel, B   At the end, P, paper tubes coated with mercury sulphide or other material could be inserted and a strong current of air or other gas directed over it from the nozzle, the air escaping at the wire gauze end.   The two electroscopes would indicate any charge acquired by the paper or carried away by the current of air, fig 3   At first small charges were indicated by both electroscopes, that
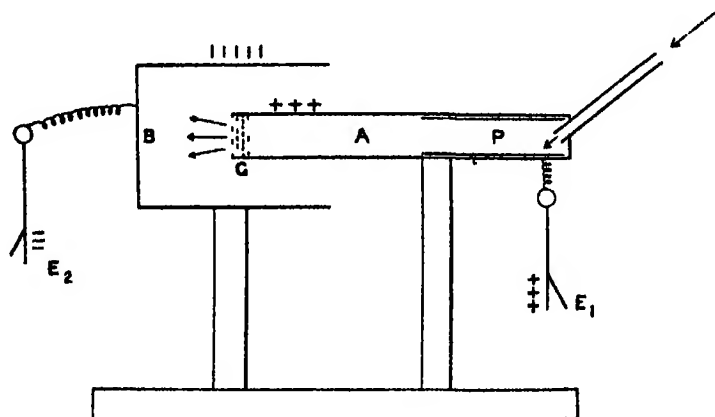
Fig 3

on the one attached to the tube being positive whilst that on the copper vessel was negative, as would be expected to be the case with mercury sulphide, but the charges were only obtained for a short time, and were clearly due to some of the material being torn off mechanically   This was confirmed by rubbing the paper after the charges had ceased, and then the detached particles gave rise to charges on blowing   The same thing occurred if hydrogen was used instead of air.   The air does not carry away a charge as a consequence of being blown over a surface of mercury sulphide or other material.

When a tube was packed with powder and the ends closed with plugs of cotton wool   no charge was carried away by the air driven through the apparatus unless some powder managed to escape through the plugs.   If the charge had been due to an effect of contact of air and dust some charge should have been obtained by this method.   It must therefore be concluded that the charges are not due to mere increase of surface of contact between the air and the dust

It was always easier to detect the charge upon the air* than upon the dust, and some determinations of the amount of electricity carried by the air and finer dust particles were made by observing the potential to which a conductor of known capacity was raised by it   The large tin-lined box used in the previous experiments was employed as a means of catching the charge upon the air   It was supported by three blocks of paraffin and a wire from the metal lining joined to an electroscope   The capacity of the arrangement was about 70 cm

On blowing in some mercury sulphide from the bottle the box became strongly charged with negative electricity, and after two puffs of air the whole apparatus was charged up to a potential of 50–60 volts   The quantity of electricity carried by the air and dust into the chamber under these circumstances was about 12 E S units, and the charge per cubic centimetre about

$$\frac{12}{45 \times 45 \times 55} = \frac{1}{10000} \text{ unit}$$

Instead of the tube from the bottle being allowed to project directly into the box an earth-connected metal tube was sometimes inserted between the two   This, however, had but a small influence on the magnitude of the charge, which seems to be generated when the dust, so to speak, suddenly expands.

A very extreme case of this kind was seen when the dust on its way to the box was passed through 20 feet of compo piping, 0 4 cm in diameter   Using cornflour for the dust a very strong charge was given to its apparatus when only a centigramme or so of the powder had been sprayed   In one instance the powder was sprayed through the 20 feet of tubing into the room, and when less than 4 cgrm. had been sprayed, the air of the room was charged to such an extent that the radium collector indicated a potential of 100 volts.   In some experiments made in a large tin vessel which could be closed air-tight it was found that the total charge upon air and dust together was zero.

It is difficult to locate the origin of the very strong charges possessed by both dust and air, and it seemed at first as though the mere act of raising the dust, and of thus increasing the area of contact between dust and air, might be sufficient to account for the charges developed, as may be done in considering the origin of the charges developed upon water spray and air, when larger drops of water are broken up into smaller ones; but it does not appear that the increase of surface of a mass of finely divided material

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* Perhaps the charge is not upon the air itself, but upon very fine particles carried along with the air, and these may not settle readily

when blown into a cloud, nor the mere friction of air against dust, is sufficient to account for the charges found upon dust and air   There remains then to be considered the case of friction of the similar dust particles against each other. Although the particles are of the same material there might easily be sufficient surface differences to permit of two particles becoming oppositely charged by rubbing against each other, and in this case it might be expected that equal charges would be generated upon the two particles which had been in contact, so that the charge upon the dust as a whole should be zero Certain experiments already referred to, however, gave indications that the charge associated with a given substance was not absolutely fixed, and the fact that the charge obtained upon a certain dust was generally independent of the nature of the gas in which it was raised, and also independent of the nature of the surface from which it was blown, led to investigations being made to ascertain whether two charges were not actually present in the dust itself

In many futile attempts to measure a saturation current through the dust-laden air it was noticed that the dust collected upon the electrodes between which it was tried to send a current, and it was further seen that one electrode became much more thickly covered with dust than the other. A number of experiments have been made with various materials to investigate this point, and the results will now be detailed.

The apparatus (fig 4) used for carrying out the experiment consisted of an inverted glass bell-jar having an opening at the bottom and covered on the top by a plate of thick zinc through which passed wires connected to two insulated cylindrical conductors   These conductors were connected to the terminals of a battery of 400 secondary cells, the central point being earthed, so that the conductors were equally and oppositely charged. Through the cork at the bottom the tube from the spraying bottle passed, and by sending in a gentle current of air through O, a mixture of air and dust passed through the apparatus, the excess escaping through X   In some cases X was closed and O connected to a bulb so that dust might be raised without any air leaving the apparatus   No particular advantage resulted from this, and the amount of dust collected upon the conductors was much smaller   In some cases a lining of earth-connected wire gauze was placed inside the bell-jar, and in fact a metal vessel is best, but it was of interest to watch the deposition of dust upon the electrodes. The electrodes were made of brass and highly polished, and were attached at the sides to the supporting rods so that by rotation they could be arranged at different distances from each other   Various voltages were applied to A and B without producing an essential difference save that of varying the rate of

collecting the dust, which gathered on all parts of the electrodes, but if these were close together, collected in greatest amount on the portions of A and B facing each other

If the electrodes were uncharged only a small amount of dust settled on them, the air escaping, however, was strongly charged, as was seen from the
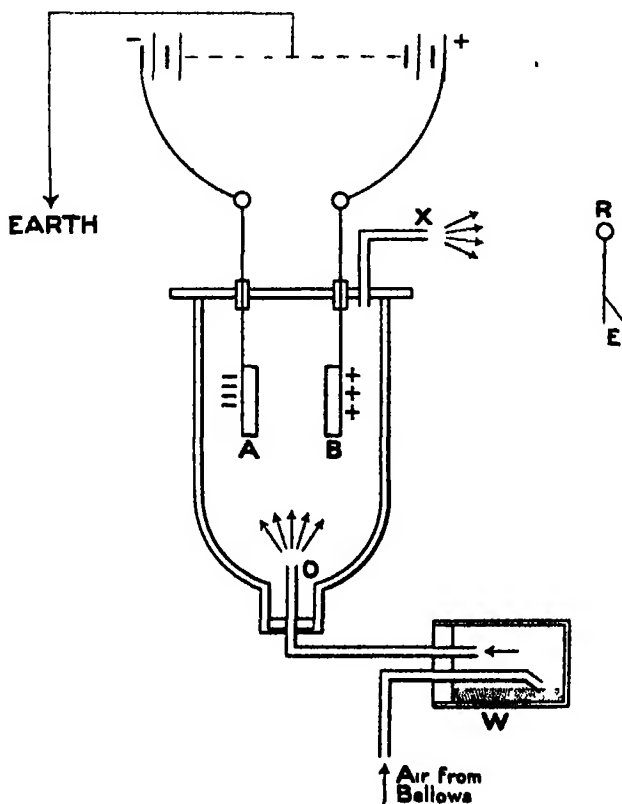
Fig 4.

electroscope connected to the radium collector placed near X. The results of some typical cases are given in Table V (p. 266).

In most cases examined there was a very marked difference in the amount of dust collected upon the electrodes, and the greater this difference the greater the charge carried away by the air   The charge carried away by the air was always opposite to that upon the electrode which attracted the greater quantity of dust.

If one can measure the amount of charge from the mass of the dust attracted to the electrode, then, if the greater quantity goes to the positive electrode, *i.e.* has a negative charge, we might expect that the air should have

Table V

Material used	Charge upon the air	Excess of dust upon—	Charge upon air
Flour	+	— electrode	Great
Fine silica	—	+	„
Mercuric sulphide	—	+	„
Red lead	+	—	„
Sulphur	—	+	„
Bismuth oxide	+	—	Small
Chalk	+	—	„
Zinc dust	—	+	Great
Iron filings	—	+	Variable
Copper oxide	+	—	Slight
Magnesium oxide	—	+	Uncertain
Molybdic acid	—	+	Very great
Mercuric oxide	+	—	Slight
Antimony	—	+	
Arsenious oxide	—	+	Great
Road dust	—	+	Variable
Coal dust	+	—	„
Portland cement	+	—	Great
Quinine	—	+	Small

a positive charge, whereas the opposite is the actual case   It is true that all the dust is not collected by the electrodes and that a further electrification is produced when the excess of dust escapes into the air surrounding the apparatus

As there was such a considerable difference in the appearance of the two electrodes after the deposition of the dust, it seemed possible that some quantitative relation might exist between the amount of dust attracted by the two electrodes, and a number of measurements were made of the actual quantity of dust deposited   If the electrodes were well polished and uncharged, the amount of dust deposited upon them in a reasonable time was practically unweighable, but if they were charged there was no difficulty in determining the weight of material upon both electrodes

The method of making the determinations was as follows —

The electrodes were well polished and weighed upon a balance to 0 1 mgrm , and after the deposition of the dust weighed again

In Table VI (1) gives the weight of the electrode before the deposition of dust, and (2) the weight afterwards. In the last column the ratio of the greater to the smaller gain in weight is given, and this is positive/negative or negative/positive according to the nature of the dust   Many observations were made but only a few are included in the table, and these are typical.

The ratio of the masses of the charged powders is not very uniform save in the cases of mercuric sulphide and cornflour , there the value is somewhat of the order of 2 : 1, but in the opposite sense as regards the signs of the

<center>Table VI.</center>

Weight of + electrode			Weight of − electrode			Ratio Gain + / Gain −
(1)	(2)	Gain	(1)	(2)	Gain	
Mercuric Sulphide						
25 9037	25 9051	0 0014	25 9072	25 9079	0 007	2 0
25 9037	25 9124	0 0087	25 9072	25 9114	0 0042	2 07
25 9037	25 9152	0 0115	25 9072	25 9127	0 0055	2 04
25 9040	25 9085	0 0045	25 9076	25 9096	0 002	2 25
Cornflour						Gain − / Gain +
25 9025	25 9156	0 0131	25 9072	25 9351	0 0279	2 1
25 9025	25 9150	0 0125	25 9072	25 9333	0 0261	2 1
Molybdic Acid						Gain + / Gain −
25 8905	25 9000	0 0095	25 9030	25 9042	0 0012	7 99
25 9040	25 9086	0 0046	25 9020	25 9051	0 0031	1 48
Red Lead.						Gain − / Gain +
25 8350	25 8380	0 003	25 8360	25 8485	0 0125	4 12
25 9032	25 9070	0 0038	25 9075	25 9320	0 0245	1 0
25 9032	25 9080	0 0048	25 9075	25 9217	0 0142	2 96

charges in the two cases   The difference in the masses was not due to a difference in the individual size of the charged particles, as far as could be determined by the microscope, but it may be that a group of particles clinging closely together might be struck by a number of smaller or individual particles, and thus acquire opposite charges, and in some cases it did seem as though the negatively charged particles shaken off the positively charged electrode were larger than the positively charged ones shaken off the negative.

An attempt was made to see whether any separation of the charged particles could be brought about by settling under gravitation, and with this object a box 120 cm. in length, 20 cm in depth, and 20 cm. in breadth was taken and three pairs of insulated electrodes inserted in the cover.   Holes at the two ends of the box allowed of a cloud being blown in at one end, and of the excess of dust escaping at the other.   The electrodes were joined in parallel to the leading wires, and were charged by a battery of small cells to a difference of potential of about 800 volts.   The respective pairs (1),

(2), (3) of the electrodes were carefully weighed, a current of dust passed through the air for a short time and the electrodes again weighed　Some of the results obtained are given in Table VII —

Table VII —Long Box Experiment　Dust used, Cornflour

First pair of electrodes		Ratio −/+	Second pair of electrodes		Ratio −/+	Third pair of electrodes		Ratio −/+
Gain in weight +	Gain in weight −		Gain in weight +	Gain in weight −		Gain in weight +	Gain in weight −	
(1) 0 026	0 ·0625	2 4	0 0078	0 048	5 5	0 ·0020	0 ·0079	4 ·0
(2) 0 ·0088	0 ·050	4 8	0 0076	0 ·032	4 2	0 0015	0 0145	9 7
(8) 0 ·0196	0 0615	3 14	0 ·0025	0 ·0268	10 7	0 002	0 017	8 5
(4) 0 0093	0 0312	3 3	0 0088	0 0454	5 0	0 0018	0 ·0060	4 ·6

In this table it is seen that the ratio of the masses of the positively charged particles to those of the negatively charged ones increases with the distance from the origin of the cloud , that is the positively charged particles travel a greater distance before settling　It may be that this is merely an accidental relation, or that the positively charged particles are finer and are carried farther　Of course, there are so many factors which could interfere that it is not safe to generalise

From the experimental details which have been given, it seems quite clear that the electrification must be due to some mutual action amongst the dust particles, such as repeated contact or the rubbing of one particle upon another　Small charges only would be produced upon the individual particles, but, as there are so many, the collective effect might well be great.　It is, of course, well known that, by rubbing together two pieces of the same material, two charges of electricity can be obtained, it being presumed that there exists naturally some slight difference between the two surfaces which are being rubbed, and no doubt many observations have been made upon the matter, but the cases recorded are few

Some experiments were therefore made to ascertain to what extent naturally occurring ordinary bodies gave rise to measurable charges of electricity when rubbed together , it appears that practically every material is found to become charged when rubbed on another piece of the same material, the two pieces becoming oppositely charged.* The charges produced are comparatively large, so that no difficulty is experienced in

* Heschus, 'Journ de la Soc. Russe Phys.-Chim.,' 1901, states that when pieces of similar material are rubbed together they become charged with the same kind of electricity, and the dust abraded has a charge of opposite sign.

detecting them with an ordinary electroscope, and very small pieces of material suffice to give measurable charges   The sign of the charge upon each piece of material is apparently fortuitous, for, given two pieces, A and B, of the same material, then A may be positive at one time and B at another, probably there is some slight surface difference, which is not permanent   Amongst the substances examined, and which readily gave the two charges when two pieces are rubbed together, are quartz, cinnabar, Iceland spar, arragonite, tourmaline, barytes, felspar, mica, fluor spar, sulphur, potassium nitrate, potassium bichromate, and oxalic acid   This list is representative, but not exhaustive, and in each case opposite charges are obtained from two pieces of the same substance   Of course, rubbing two pieces of dissimilar substance also gives rise to two charges.

It is very surprising what small amounts of material will acquire measurable charges   Pieces of cinnabar not more than 0 1 sq cm in area give very definite charges

In addition to the charges upon the materials, some charge is also given to the air surrounding the material, and the sign of this charge depends upon the nature of the material   Thus, by rubbing two rhombs of calcite together inside a box in which was present an insulated wire coated with radium and connected to an electrometer, the latter indicated that a positive charge had been gained by the wire, but if two crystals of quartz were used, then the charge was found to be negative   This agrees with the signs of the charges given to air during the raising of a dust cloud of these materials.   These charges upon the air were not very strong, but quite definite, especially in the case of calcite, when the sign was always positive. It is most probable that small particles are abraded during the rubbing, and these may give a charge to the air, and it is possible that in all cases the charge upon the air is really due to very fine particles which do not readily settle, or which move with such velocity that they escape capture by the charged electrodes used in certain of the experiments

Some examples of the electrification produced by rubbing crystals together are now given.

Quartz upon Quartz

Large crystal	Charge	Small crystal	Charge
Pyramid face (1)	+	Pyramid face (1)	−
Prism „ (1)	+	Pyramid „ (1)	−
Prism „ (1)	+	Prism „ (1)	−
Pyramid „ (8)	+	Pyramid „ (2)	−
Prism „ (2)	+	Prism „ (8)	−

In this series the large crystal was always charged positively, but, on repeating the experiment later, the reverse was seen   The electrification is independent of the orientation of the crystal faces

The large crystal was then used to rub other quartz crystals, and it generally acquired the same charge.   With "smoky" quartz only a very feeble charge could be obtained

In crystals of quartz there is a distinct difference in the nature of the surface of the prism and the pyramid faces, and it might have been expected that some difference in the charges would have been noted, but this was not the case.   Iceland spar is, however, a simpler crystal, and one which has fewer faces, and the six faces are mineralogically the same.   A large crystal of Iceland spar was broken into pieces and two fair-sized rhombs selected for experiment   These were rubbed on each other in a definite order so as to bring the different faces successively into use.   A number of experiments was made with each face, allowing a short interval between each rubbing   One crystal generally remained positive with reference to the other, quite independently of the particular faces used, but occasionally a reversal occurred, and, by allowing the crystals to rest for some time, the one formerly positive might now be negative   As with quartz, the charge upon the crystal was independent of the orientation

A crystal of arragonite was rubbed on one of calcite, varying the faces used. In every case the arragonite was positive to calcite

A few cases of mixed crystal are now given —

Arragonite	+	Calcite	—
Fluor spar	+	Calcite	
Tourmaline	+	Calcite	—
Barytes	+	Calcite	—
Quartz	+	Calcite	—
Barytes	—	Quartz	+
Felspar	—	Quartz	+
Felspar	+	Calcite	-

A couple of "worked" quartz plates were found to be most efficient   The temperature of the plates was varied and the electrification observed, and the sign of the electrification is apparently not affected by the initial temperature of the two plates, which would soon be equalised by contact

Plate A		Plate B	
Cold	+	Cold	—
Hot	—	Cold	+
Cold	—	Cold	+
Hot	—	Cold	+
Cold	+	Cold	—
Cold	—	Hot	+

Plate A		Plate B	
Hot	+	Hot	−
Cold	+	Hot	−
Hot	−	Hot	+
Hot	−	Hot	+
Cold	−	Hot	+
Hot	+	Cold	−

In general, naturally occurring crystals of material are the most suitable to employ, because the surfaces are fairly definite in condition, and also because they are better insulators than pieces of amorphous material   The sign of the electrification acquired appears to be quite fortuitous

The facts as revealed by the experiments are very difficult to interpret. At present it seems quite definite that the charges originate in the powder itself, that is, there must be friction or contact between the various particles, which differ in size or surface condition, in such manner, that two groups of oppositely charged particles are yielded by the dust from chemically homogeneous materials, and also that the air or gas used to raise the cloud either becomes itself electrified, or else carries with it very fine charged particles of the material   The total electrification of the two sets of charged particles and the air accompanying them is zero.   The nature of the gas used to raise the cloud does not seem to be of much importance

It was suggested to the writer that it might be possible to obtain some evidence of the presence of double layers surrounding the particles of dust, and to attempt their removal, but the experimental difficulties seem at present to be insurmountable   Some work was done in this direction by heating precipitated silica for some time in an exhausted tube, and then after cooling raising a cloud by shaking   Charges were, of course, obtained, but it was not possible to distinguish between those due to the agitation of the dust particles amongst each other, and those due to friction of the dust against the walls of the containing vessel.

Summary

(1) The results of these experiments confirm generally those given in the former paper

(2) The raising of a cloud of dust is accompanied by the production of large charges of electricity   Some of the dust particles have positive charges, and others negative

Either one set of charged particles settles rapidly, leaving the other set in the air, or else a charge is given to the air itself *   The charge is retained by the air for some considerable time.

* The experiments do not show which of these views is correct.

(3) The sign of the charge remaining, in the air depends upon the nature of the material used "Acidic" bodies, such as finely divided silica or molybdic acid, give to the air a negative charge, whilst "basic" bodies, such as lead oxide, or organic dusts, such as flour or coal, give a positive charge

(4) The total electrification of dust and air is zero

(5) The friction between particles of similar material apparently produces sufficient electrification to account for the charges observed

(6) An unweighable amount of dust can produce an easily measurable charge

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The Electrical Ignition of Gaseous Mixtures

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CONTENTS

1. Introduction.

The ignition of explosive gaseous mixtures for experimental purposes is generally made by an electric spark or train of sparks between fixed

terminals.   The temperature of inflammation cannot in this case be measured, and it is determined by that of a hot surface in contact with the gas, or by calculation from its adiabatic compression   The fact that there is a critical temperature of ignition and that the velocity of an explosion wave can be calculated from the thermal constants of the gas and air, has led to the view that the process is a thermal one throughout, with in general two stages, a period of slow combustion and rise of temperature, and the true explosion on this reaching a certain limiting value.   There is, however, a more intimate possible cause of the division of the molecule of combustible gas which precedes explosive combination   Recent work on the ionisation of gases has made familiar the view that a molecule can be ionised by corpuscular radiation, and that by the gain or loss of such corpuscles the nature of the molecule can be profoundly modified   The present paper is an examination of certain typical gases and vapours for the purpose of finding evidence of the mechanism of the process by which the energy of the source is transferred to the gas at the moment of ignition

A very full report on gaseous combustion was given by Prof W A Bone at the Sheffield meeting of the British Association, in the discussion upon which Sir J J. Thomson called attention to the possible influence of electrons in preparing the way for an explosion wave by ionising the gas *   Following this suggestion an important series of observations on gaseous ignitions has been recently made by my colleague, Mr J R. Thompson †   He found that it is possible to ignite a cold explosive mixture by the incidence of X-rays on a platinum surface in it, and that when the source of ignition is a hot platinum wire an explosion is started at that temperature at which ions are discharged from the metal.   These observations, if they do not decide the ionic origin of gaseous explosions in general, prove that ionisation and explosion are intimately connected.

Direct evidence of the kind of electrical action which starts a gaseous explosion under normal conditions is given by the difference between the igniting powers of continuous and alternating current break-sparks   If ignition were a simple thermal process, the igniting power, measured by varying some non-electrical factor, such as the percentage of combustible gas in the mixture, and finding the corresponding variation of the least igniting current, should be proportional to the square of the current in the circuit, whether continuous or alternating, other conditions being the same.

* 'Brit. Assoc. Rep.,' 1910, p 501.
† 'Phys. Zeitschr,' vol 14, pp. 11–15, Jan 1, 1913, and 'Science Abstr.,' No 631, vol. 16, part 4, April 13, 1913.

But when the current is alternating. the present experiments show that the energy of the circuit required to ignite gas is much greater than when the current is continuous, in the case of methane 56 times greater at 200 volts, the igniting effect is therefore not simply thermal   Again, the current in a metallic circuit is proportional to the number of free electrons passing per second   When the current is broken, these are projected into the break-spark by the electric gradient at the moment of break, and a small volume of the gas in their immediate neighbourhood is ionised by them   If the igniting power of the current is ionic it should then be proportional to the current, when this is unidirectional, and this is found to be the case in many gases over an important part of their working range of inflammability.

The differences between continuous and alternating current are not only in the magnitudes of the effects, but in the manner of development of the curves in a series of related gases, for example, figs 2 and 11 for the paraffins

The general conclusion of a previous paper* on this subject was that ignition by continuous current break-sparks depends mostly upon the nature of the arc, that by alternating current on the nature of the gas

2 *Experimental Details*

Method —The explosion vessel having been filled with a gaseous mixture of the desired percentage strength, the poles are brought into contact and separated quickly, with a pause of about a second between each trial   When the current broken is from 10 to 20 per cent above the least igniting current an ignition is obtained at the first or second break, and when from 2·5 to 5 per cent below the minimum, no ignition is obtained, however many breaks are made, except in the case of some less volatile compounds in which prolonged sparking lowers the igniting current   In the present work the least igniting current was taken to be that which caused an explosion at about the fifth break. The black spots on the curves of results are the observed least values   These are not the means of a number of determinations, but give the least value reached in any case   They are correct within 2 per cent ; the slight variations in the state of the contact rods prevent closer approximation. A fresh charge of any mixture was taken after 20 sparks had been made in it without ignition

In the earliest trials the process of " trial and error " as the minimum was approached was lengthy, but after the two characteristic types of current-percentage curves had been found, a single point served to fix the position of the curve, and it is now possible to determine one such curve a day.

* "The Ignition of Coal Gas and Methane by Momentary Electric Arcs," W. M. Thornton, ' Inst Mining Engineers Trans.,' vol. 44, part 1, pp. 145–174, Oct. 12, 1912.

Explosion Vessel—For most of the experimental work it was found convenient to use a glass explosion vessel $2\frac{1}{4}$ inches diameter, 5 inches long, with ends joined to $\frac{3}{8}$ inch tubes, and having two transverse arms $\frac{5}{8}$ inch diameter, fitted with corks through which the terminal poles passed. These were of iron, copper, or nickel, bent to cross at right angles, giving a point contact which could be renewed by sliding the rods along, and by making contact on the other side of the fixed rod. The break was made by rotating one rod through a right angle.

Rate of Break—The duration of the arc at break, observed photographically by focussing it on a sensitive film attached to a revolving drum, was found to depend, in the same gaseous mixture, chiefly upon the voltage and the material of the poles. The rate of break had a nearly constant value of 12 cm a second. Except at very slow breaks, from 1 to 2 cm a second, differences in the rate of break by hand had no measurable influence upon the current which, when broken, just ignited the mixture. In every case the mixture before explosion was at atmospheric pressure and in most cases at atmospheric temperature.

Material of Poles—In the previous work, iron and copper poles were used for the purpose of examining the influence of a break of armoured electric cable in coal mining, and nickel, because of its general use in sparking plugs of internal combustion engines. In the present work, iron rods were used throughout, having a diameter of 0 1 inch.

3 *Dependence of Continuous Igniting Current upon Voltage*

The higher the voltage the less the current required for ignition. The curves obtained, of which fig 1 is an example, closely resemble the characteristics of steady arcs, which are known to be maintained by ionised vapour between the poles, and they have the same form at all percentages within the inflammable limits.

4. *Relation of Current to Percentage of Combustible Gas in Mixture*

The results in the preceding paragraph are of the same type for all the gases examined. We now consider the influence of varying the proportion of vapour in a series of gases, the chemical constitutions of which are closely related.

Paraffin Series—The lower limit of inflammability is very sharply marked in all gaseous mixtures. Many have been carefully examined by Le Chatelier and Boudouard,[*] and the paraffin series more accurately by Burgess and

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[*] Le Chatelier et Boudouard, "Sur les Limites d'Inflammabilité des Vapeurs," 'Comptes Rendus,' vol. 126, p. 1510 (1897)

Wheeler * I am informed by Dr. Wheeler that he has found the upper limits to be equally sharp, and am permitted to quote the following values
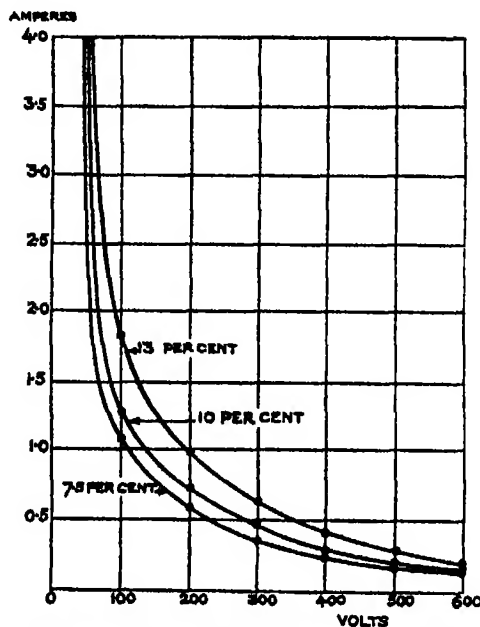
FIG 1.—Variation of least igniting continuous current with voltage on circuit
Methane   Iron poles

for them, expressed in percentage volume of combustible gas in the mixture with air —

Table I.

	Lower limit	Upper limit
Methane	5 60	14 80
Ethane	8 10	10 70
Propane	2 17	7 35
Butane	1 65	5 70
Pentane	1 35	4 50

Between these limits there has not been hitherto any means of observing directly the inflammability of the mixture, other than by its velocity of explosion   In fig 2 are given curves of igniting current for the paraffin gases by the break-spark method, from which it will be seen that the change of susceptibility to ignition varies with the percentage of gas in the same

* "The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air," by M. J Burgess and R V Wheeler, 'Chem. Soc. Journ.,' vol 99, p. 2013 (1911),

manner for all the gases examined. The curves have each three distinct portions, that which gives the peculiar form being a straight line passing through, or nearly through, zero, and expressing the fact that over the greater part of the range of inflammability the least igniting current is very closely proportional to the number of molecules of combustible gas in unit volume of the mixture At the lower limit there is a steep branch indicating that the transition from the most inflammable mixture to that which cannot
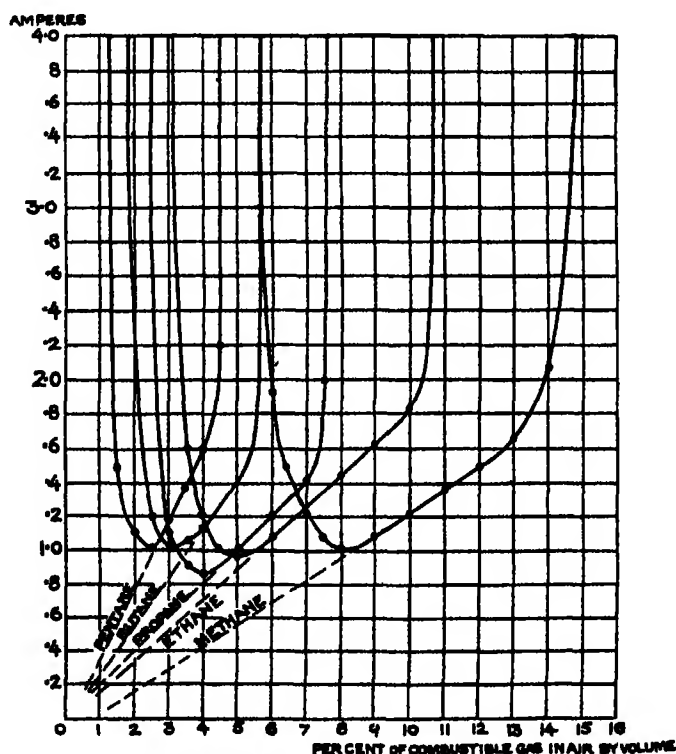
Fig 2 —Least igniting currents for the paraffin gases in air   Continuous current.
Iron poles   100 volts.

be ignited is sudden. The upper limit is approached rather more gradually. The fact that the projection of the straight base lines passes through zero proves that the igniting current is proportional to the absolute number of molecules, not merely to the change of percentage.

The gases were very pure. Pentane was prepared by drawing dried air through a wash bottle containing pure Kahlbaum isopentane heated to 27° C. The methane, ethane, propane, and butane were very kindly prepared for me by Mr. T. F E. Rhead, M Sc , under Dr Wheeler's direction,

using the methods given in the paper on the lower limit of inflammability They had the following analyses :—

Methane—$CH_4 = 98$ per cent, 2 per cent nitrogen   Ratio contraction C to absorption A on explosion = 2 (ratio for CH_4 = 2)

Ethane—$C_2H_6 = 100$ per cent   Ratio C/A on explosion = 1 245 (ratio for $C_2H_6 = 1 250$)

Propane—$C_3H_8 = 99 7$ per cent   Ratio C/A = 1·01 (ratio for C_3H_8 = 1)

Butane—$C_4H_{10} = 100$ per cent.   Ratio C/A = 0 871 (ratio for $C_4H_{10} = 0·875$)

The limits of inflammability found agree well with those given above, but no attempt was made to find the limits within a small percentage   The run of the curves from the observed points is a sufficiently close check for our purpose   The tendency of the break-spark ignition would appear to be to lower both the upper and lower limits   The most remarkable feature of the family of curves in fig 2 is that the same igniting current, that is the same energy, is required for each most inflammable mixture, in spite of the great difference in the calorific values of methane and pentane   The next is that there is no square law, except at the limiting mixtures.   The third that the most inflammable mixture is not always that in the proportions required for perfect combustion, but a mixture in which the air is in excess

The more symmetrically the molecule is bonded the closer the coincidence, as shown in Table II , n_H is the number of hydrogen atoms in a molecule of combustible gas, n_{O+H} the total atoms

<div align="center">Table II —Ignition by Continuous Current</div>

Gas	Most inflammable mixture, p_m	Mixture for perfect combustion to CO_2	$p_m \times n_H$	$p_m \times n_{O+H}$
	per cent	per cent		
Methane	8 0	9 5	32 ·0	40 ·0
Ethane	5 ·1	5 ·5	30 6	40 8
Propane	3 ·9	3 ·96	31 2	42 9
Butane	3 1	3 ·07	31 ·0	43 4
Pentane	2 5	2 51	30 ·0	42 5

5 Influence of Number of Atoms in the Molecule upon Igniting Current.

It is safe to say on the electronic theory of conduction in metals that since the minimum igniting current is the same in every gas of the paraffin series, the same number of electrons must be discharged into the mixture. The position of each curve in the figure depends on the slope of the base line, that is on the ratio I/p, where I is the igniting current and p the

percentage of gas in the mixture This slope is not proportional to the molecular weight or to the heat of combustion If the first step in electric ignition is a direct ionic attack upon the atoms in a molecule, there should be a definite relationship between the igniting current, considered as a source of ions, and the *number of atoms* either in the molecule of combustible gas or in unit volume The ratio I/p is found to be nearly proportional to the number of hydrogen atoms in the molecule, and since hydrogen is the most easily ionised of all gaseous molecules it is at least conceivable that if the effect is due to ionisation the ignition of the complex molecule of combustible gas is started by the ionisation of its hydrogen atoms, and that in its disintegration the first compounds formed are those of hydrogen and oxygen This is in agreement with Prof H B Dixon's conclusion[*] that it is during the "preflame" period of ignition which precedes the true explosion that water vapour influences the rate of propagation Any "preferential" action of hydrogen and oxygen prior to the formation of carbon products will be exceedingly rapid, and is probably beyond analysis

Writing $I/p = kn$, where n is the number of atoms in a molecule and k a constant, the relative values of k are given in Table III for the hydrogen and carbon atoms, the total atoms in the molecule, and the oxygen atoms required for perfect combustion N is the number of atoms in an "explosive unit" (see § 11), k is the current per atom of combustible gas per unit percentage mixture.

Table III

| Gas | I/p | K ($= I/pn$) × 100 | | | | N (see Table IV) |
		Hydrogen	Carbon	C + H	Oxygen for perfect combustion	
Methane	0 12	30	120	24	30	13 3
Ethane	0 18	30	90	22	26	12 0
Propane	0 22	27	73	20	22	10 5
Butane	0 28	28	70	20	21	10 4
Pentane	0 40	33	80	23	25	9 7

The outstanding result in the continuous current ignition of the paraffin series is that each gas has the same minimum igniting current The mixtures at which this occurs are in most cases near those for perfect combustion, and though it is clear that combustion is an important factor even in the initial

* "The Initiation and Propagation of Explosions," 'Chem. Soc. Journ.,' vol. 99, pp. 589–599, April, 1911.

stage, yet there is evidence that the influence of the discharge from the spark, whatever its nature may be, acts directly upon the atoms in a molecule rather than upon the molecules as a whole.

6. *The Alcohols*

The curves of fig 3 for methyl and ethyl alcohol are the same in type as for the paraffins, having a straight base inclined towards the origin   The limits of inflammability are, from the curves, 5 and 21 per cent for methyl alcohol, 3 and 8·4 per cent for ethyl alcohol.   The most inflammable mixtures
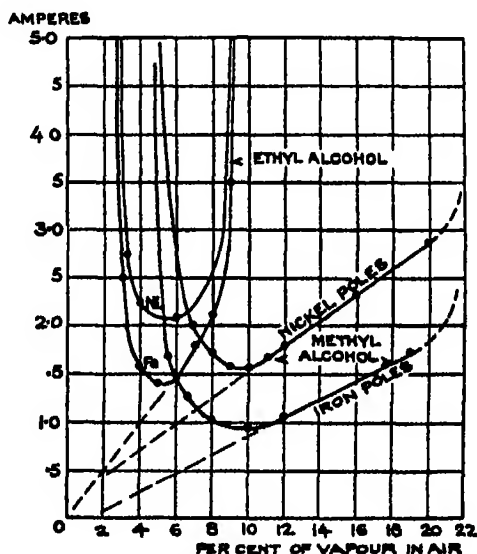
Fig 3 —Least igniting currents of alcohol vapour   Continuous current.   Iron and nickel poles.   100 volts

are at 9 7 and 5 6 per cent. for methyl and ethyl alcohol respectively , the corresponding mixtures for complete combustion to CO_2 are at 12 3 and 5 68 per cent   The alcohols therefore agree with the paraffins in their general mode of ignition by continuous current.

The slope I/p of the base is slightly decreased by the addition of the oxygen atom to the paraffin molecule, so that the inflammability of the vapour measured by this slope is lower   There is also the very interesting fact that both with iron and nickel poles the alcohol of greater molecular weight requires more current for ignition, in this respect resembling the family of curves for alternating current given in fig. 11.   There is further similarity in the more rounded form of the curves.   In this case we see again that the ratio I/p is proportional to the number of atoms n_{C+H} of combustible

gas in the molecule more nearly than to the calorific value, for the hydrogen atoms its values are 0 032 and 0 036, for the carbon and hydrogen together 0 026 and 0 027.

7 *Benzene*

The curve for benzene (C_6H_6), fig 4, differs in important features from the preceding. It has no straight part and is nearly symmetrical within the
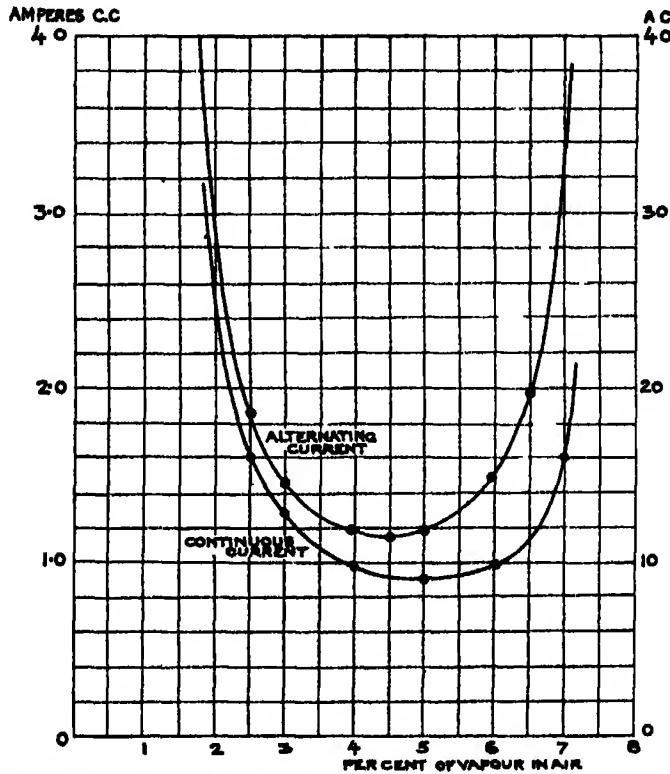
Fig 4 —Least igniting currents of benzene vapour   Continuous current, 100 volts. Alternating, 200 volts, 36 ~   Iron poles.

limits of 1 24 and 6 37 per cent found by Sorel* for pure benzene   The most sensitive mixture is about 4 8 per cent, that for perfect combustion 2 73 per cent   There is clearly no relation between the latter and the shape of the curve, but the point of combustion to carbon monoxide is 4 47 per cent.   The same form and position of the benzene curve is found when the current is alternating as when continuous.   The evidence is therefore strong that in so far as the magnitude of the igniting current is an

* 'Carburetting and Combustion in Alcohol Engines,' by E. Sorel, trans. Woodward and Preston, p 53.

indication of the atomic changes occurring at the instant of explosion, carbon monoxide is the chief and first product of combustion, and the formation of carbon dioxide is in this case a much slower process than in lighter gases   Dixon has shown that combustion to carbon monoxide followed by burning to carbon dioxide is characteristic of the explosion of many gases.   The evidence given here from the circumstances of electrical ignition shows that it is much easier to ignite benzene vapour when it burns to carbon monoxide than to carbon dioxide   This is the reverse of carbon disulphide and hydrogen, where the most inflammable mixture is that giving perfect combustion   The benzene molecule is much more complex than either of these, and it would be interesting to examine the influence of complexity upon the type of ignition   Pentane has little left of the straight line base

The after-burning of benzene may be the reason why benzol fuel gives less shock than petrol · the combustion is not so sudden and is more extended over the stroke , the minimum igniting current, 0 9 ampère, is however much the same as pentane, in this respect differing greatly from carbon disulphide, the next vapour considered

8   *Disulphide of Carbon*

This liquid is always found in commercial benzol and possibly plays an important part in the ignition of rich mixtures, for as shown by the curve of fig 5, the vapour is inflammable within wide limits of mixture with air. The liquid boils at 46 2° C and the explosive mixtures were prepared by heating the liquid over mercury in a containing vessel and drawing a measured volume of pure gas into the explosion vessel, which was heated to prevent condensation on the glass or mercury piston.   The limits, from 2 per cent to 45–50 per cent , are only approximate, but the curve has the same features characteristic of continuous current ignition of the paraffins and alcohols

The most interesting points about it are the exceedingly small igniting current, 0 32 ampère, and the fact that the point for perfect combustion is nearly the most inflammable mixture · this is at 6 5 per cent   The sensitiveness of carbon disulphide to ignition by break-sparks is in agreement with Hemptinne's observation that detonating mixtures of it with oxygen are explosive at much lower pressures than most gases, the limiting pressure being about 13 mm.

The discharge tube of glass from the explosion vessel became rapidly coated with sulphur after the ignition, suggesting a high state of atomic dissociation of the combining gas during the explosion   It was suggested by my colleague,

Dr J. A. Smythe, that carbon disulphide being an endothermic compound, the supply of heat to it by the combustion of a small portion of the mixture

Fig 5 —Least igniting currents of carbon disulphide vapour   Continuous current, 100 volts.   Alternating, 200 volts, 36 ~   Iron poles

or from the arc might cause the rest to explode with liberation of free carbon and sulphur.

The explosion is violent at all percentages

9 *Hydrogen and Carbon Monoxide.*

Fig 6   In the ignition of hydrogen by continuous current break-sparks the current is found to be the same in all strengths of mixture except towards the limits of inflammability   The ignition is therefore an isolated molecular process, independent of concentration, requiring only a certain intensity of molecular movement to be produced   From the thermal point of view this would mean a certain critical temperature in the spark, from the corpuscular radiation standpoint a certain energy of projection from it.
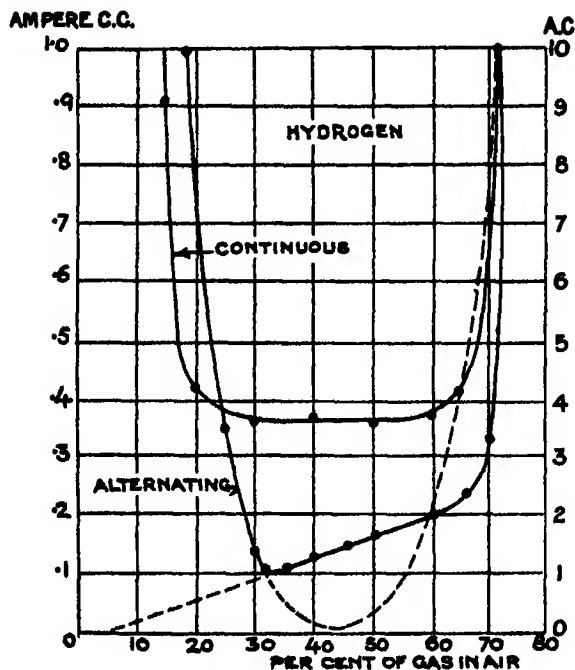
Fɪɢ 6 —Least igniting currents of hydrogen in air   Continuous current, 100 volts
Alternating, 200 volts, 36 ~   Iron poles

[*April* 8*th*, 1914 —Carbon monoxide, fig 7, differs from hydrogen in that the continuous current curve is slightly inclined, and the alternating current curve horizontal   These two curves show, as it were, the genesis of the straight line type from a parabola symmetrical between the limits of inflammability]

10   *Influence of Circuit Voltage on Form of Curves*

All the previous work has been done with a circuit voltage of 100   The influence of varying the voltage is to change the slope of the base in a regular and rapid manner, fig 8

Voltage .	50	75	100	125
Slope of base .. .	0 472	0 222	0 119	0 0468

The variation is approximately as the cube of the voltage, and is such that at voltages over 100 the igniting current is nearly the same over the whole range of inflammability, a point of importance in the working of internal combustion engines   The circuit voltage has no influence on the position of the point of greatest inflammability.
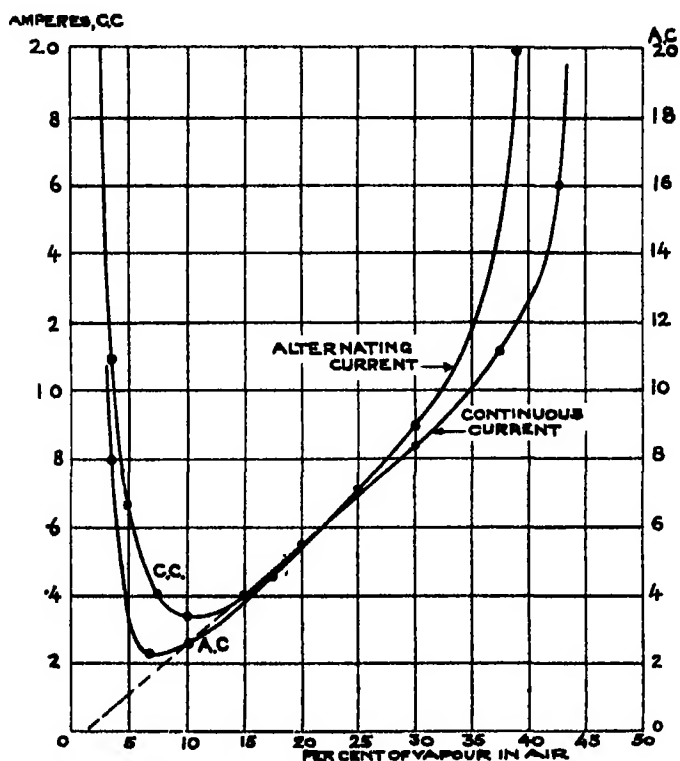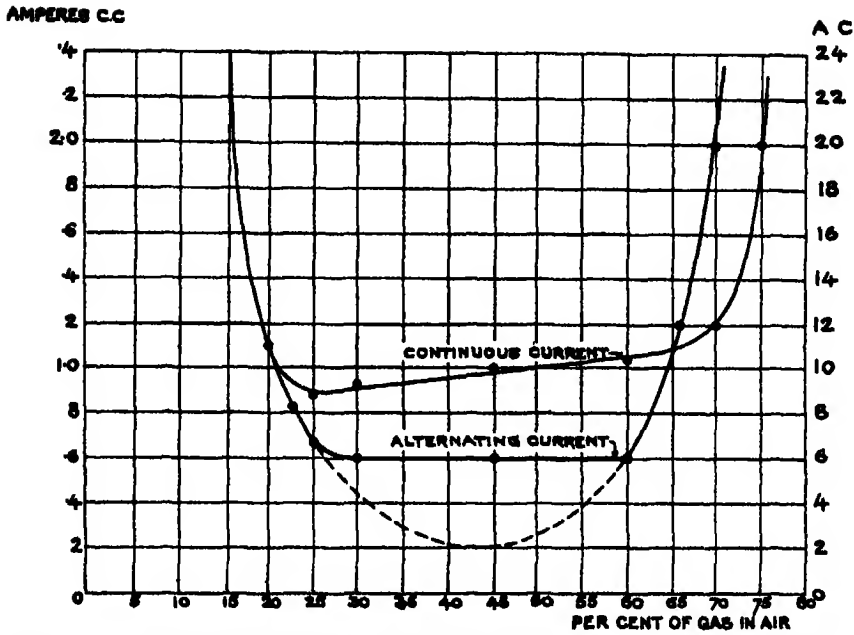
Fig 7 —Least igniting currents of carbon monoxide in air   Continuous current,
100 volts   Alternating, 200 volts, 36 ~   Iron poles
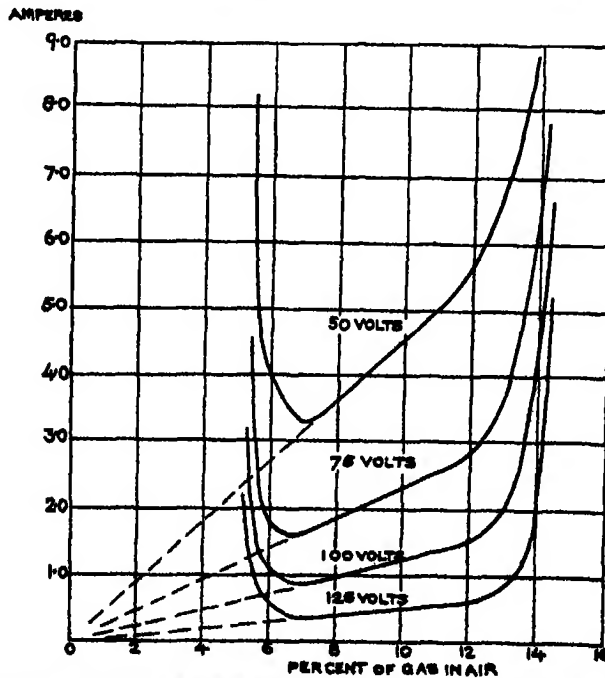
Fig. 8.—Influence of circuit voltage on least igniting current in different percentage
mixtures of methane and air.   Iron poles, continuous current

11. " *Time of Explosion.*"

The paraffin molecule is in general heavy and complex, and a number of oxygen molecules sufficient to form the products of combustion must surround it at the moment of disintegration   This group of gas and oxygen molecules may be called the *explosive unit*, and the number of such in unit volume is proportional to the percentage strength of the mixture The time of explosion T depends on the number of such units per cubic centimetre, and on the mass per unit volume of inert gas which transmits energy without raising it   The minimum time of explosion is to be found in that mixture in which the retarding influence of excess molecules which cannot enter into full combination is balanced by the accelerating influence of the energy set free by their partial combustion   If from this point the rate of explosion falls in proportion to the increase in the mass of inert gas, and the number of explosive units is diminished in the same proportion, it follows that T will vary as the square of the change   This is true as long as the units are so close that the space between them is not great compared with their volume after explosion, but forms as it were a shell around each   As the limits of inflammation are approached they are so far apart that the inert gas forms a sphere around each unit and the explosive unit is small compared with the volume of inert gas   The change of inert mass then varies as the square of the distance between the units and the time of explosion as the cube of the change of percentage   [The rate of change of the volume of a sphere varies as the square of its radius]   The period known as the time of explosion would thus appear to be capable of a simple mechanical explanation.   The square law followed by petrol indicates that the explosive unit is in that case large compared with the mass of inert gas, as indeed it is known to be, and the above argument may explain why simple gases have higher limits of inflammability because of the smaller volume and mass of the explosive unit.

The shape of the curves connecting alternating igniting current and percentage strength of mixture has probably the same origin   They are, in the more regular gases—the paraffins for example—parabolic at the minimum and cubic towards the limits

12. *Ignition by Alternating Currents*

The curves expressing the experimental relation between voltage and igniting currents, and between current at different frequencies and percentage of gas, are essentially different in type from those given above for direct

currents. Consider first the ignition of the mixture of methane and air just giving complete combustion.

Voltage, Current, and Frequency.—At all voltages much larger currents are required to produce ignition than with direct current Below 100 volts the currents are very large, from 200 to 600 volts are nearly constant, and at some point above this rapidly fall, to about 0 2 ampère at 2000 volts Thus, in places where electricity is used in the possible presence of inflammable mixtures, as, for example, in coal mines, alternating currents are much safer than continuous, where open sparking may occur, and the higher the frequency (up to 100) the greater the safety The igniting current at 200 volts with continuous voltage is 0 5 ampère, with alternating current at 200 volts and 100 periods per second the least igniting current is 20 ampères. This is the root-mean-square value and is given in the curves, but the ignitions are always obtained from sparks giving the maximum flash, that is when the circuit is broken at the crest value of 28 ampères The arrangement of the resistance and inductance of the circuit was the same as that used with
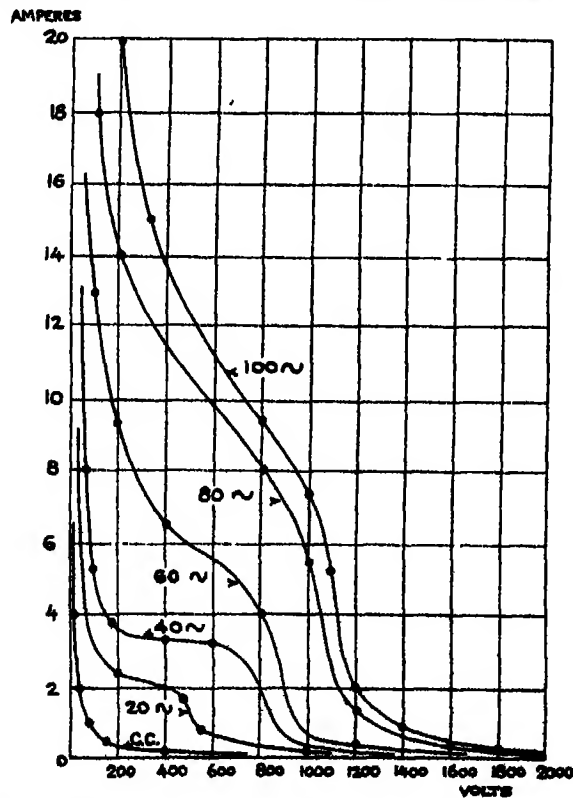
Fig. 9.—Influence of frequency in igniting current in a 9 5-per-cent mixture of methane and air Iron poles, alternating current

continuous currents, so that the energy of any one spark is proportional to the current, not to its square   The alternating igniting current at this voltage is 56 times greater than the least continuous current at the same voltage, and the difference shows beyond doubt that the energy of the continuous current spark is not transmitted thermally to the gas, for in that case the energies of ignition in the two cases should be the same   The shape of the curve of fig 9, similar to the isothermals of vapours below the critical temperature, suggests that one of the factors in the electric circuit may become critical. It is clear that it can only be a time effect, and that time must play an important part in the phenomena of ignition   The horizontal part of the curve disappears, as shown, both at high and low frequencies, for at the highest frequencies it is practically a continuous arc, and at the lower it approximates to the direct current hyperbolic type   At moderate frequencies the arc in reversing strikes across the ionised vapour in the break gap and may persist for several periods   If the break occurs in less than 0 05 second—the minimum time of ignition—the critical change of energy in the gas may never pass into the explosion stage   There should then be some period at which the remarkable influence of frequency reaches a maximum   The highest frequency in the present case at which it was possible to make measurements was 100 a second, and it is seen from fig 10 that the maximum is being here approached   At frequencies of several hundred periods per second ignition will no doubt be obtained by
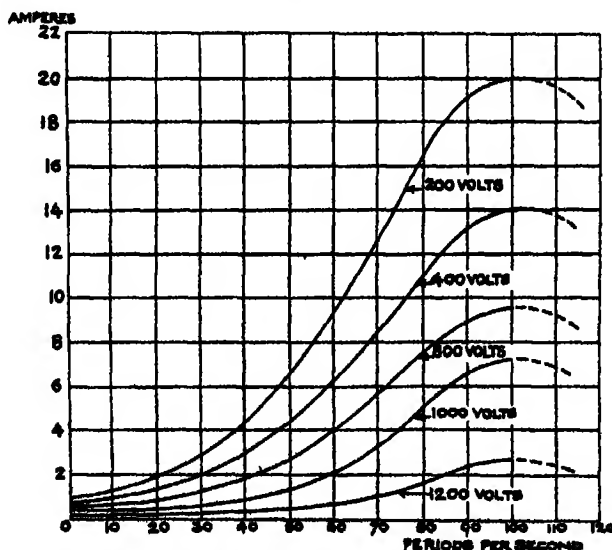
Fig 10 —9 5-per-cent. mixture of methane and air, most difficult to ignite at
100 periods per second. Iron poles, alternating current.

smaller currents   The curves are of the usual trial and error type and
show that the approach to the maximum is a statistical one, but the effect
of raising the frequency is to avoid, as far as possible, the ignition of the
gas and the curves would be symmetrical about the point of maximum
difficulty of ignition   If the ignition of a gaseous mixture is a thermal
process alone the frequency of the current should have no effect as distinct
from the energy of the spark, but it has, in fact, an exceedingly great influence
on the magnitude of the current required to be broken, an influence which
can only be accounted for by the rapid alternation of the voltage between
the poles preventing the free escape of ions from the spark

   There is again one frequency at which the horizontal portion of the curve
is longest   This is when the frequency is about 50, and is much more marked
when the poles are nickel *   An approximation to the form of the curve is
obtained by considering the ordinates to be inversely proportional, not to the
voltage alone as in fig 1, but to the product of the voltage and the time of
duration of the break-spark   At low voltages this duration is directly pro-
portional to the voltage, it then reaches a maximum, falls over a long range
of voltage and rises again as the gradient becomes so great that the air in the
gap is ionised by it alone   For direct currents $I = a/V$ where a is a constant ,
writing for alternating currents $I = a/VS$, where S is the duration of the
spark, the igniting current will vary little from B to C, fig 11, if it
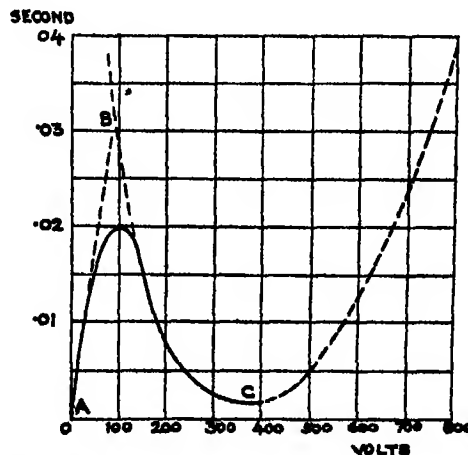
Fig 11 —Influence of voltage on duration of continuous current break-sparks in
methane, 9·5 per cent   Circuit non-inductive.   Iron poles.

depends on the product   This product is known to be constant for a portion
of the steady continuous current arc characteristic   When S is directly

* "The Ignition of Coal Gas and Methane by Momentary Electric Arcs," *loc. cit* , fig 16

proportional to V, as from A to B, IV^2 is constant, and as S rises again above C, I falls in the same direction as before towards the horizontal axis. When the voltage is high enough to strike a continuous stream of sparks between the poles when separating, S is infinitely large.

The time of duration depends on the inductance of the circuit. In all these alternating current experiments the circuit was non-inductive, that is the power-factor was never less than 0 95, and the currents had a pure sine wave form.

13 *Relation of Igniting Current to Percentage of Gas in Mixture*

Paraffin Series—Working with alternating current more trials are required than with continuous currents to obtain the least igniting current, for the poles may be separated at a value approaching zero, or at a crest value of the current. In the one case there is no arc, in the other it is at a maximum. The final critical igniting current is, however, little affected by the uncertainty of break

The curves of fig 12 obtained for the paraffin gases are remarkably uniform
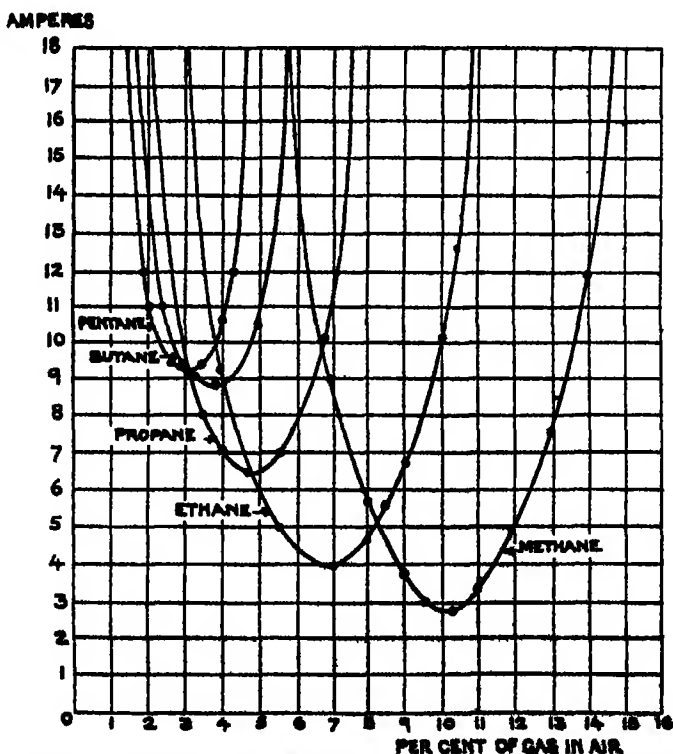
FIG 12—Least igniting currents for the paraffin gases in air. Alternating current, 200 volts, 36 ~. Iron poles.

in type and fit closely into a regular scheme   Their most striking feature is that the higher hydrocarbons are the most difficult to ignite by break-sparks, a fact which must profoundly affect our measure of inflammability.   They can be ignited in weaker mixtures, but not so readily   Pentane takes three times more energy to ignite by alternating currents than methane.   Another interesting feature is that the curves are as nearly as possible symmetrical between their upper and lower limits of inflammability, the maximum inflammability being at the mean of the extremes   In the family of curves for continuous current in fig 2 the minimum currents are the same throughout, in that for alternating currents in fig 12 *the product of the minimum current and the percentage at which it is found is the same for every gas,* as shown in Column 7, Table IV   The heat of combustion of pentane is four times greater than that of methane and it cannot be suggested that the gas is more difficult to ignite because of its greater heat of combustion, for the alternating igniting currents of ethyl and methyl alcohol are the same, fig 13
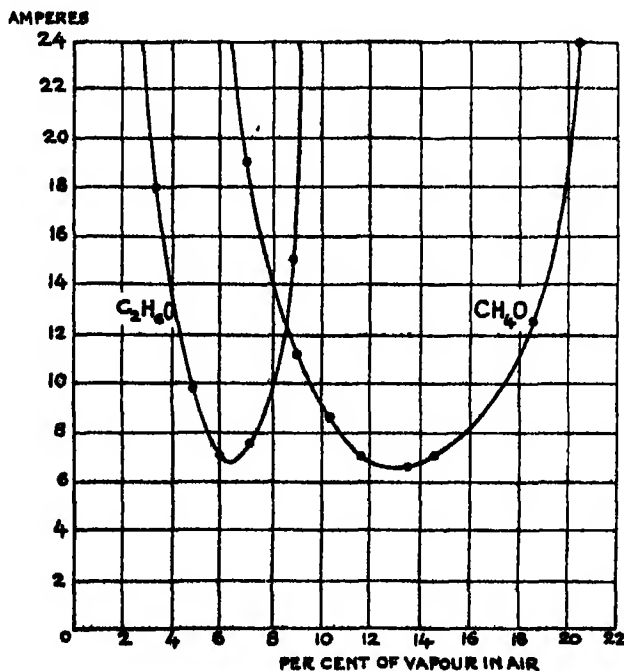
Fig 13 —Least igniting currents for alcohol   200 volts, 36 ~   Iron poles

14. *Atomic Nature of Break-spark Ignition.*

But if it is true that combustion is the formation into more stable compounds of molecules electrically unsaturated and that no combination takes place until they are ionised either wholly or in part, it would follow

that the igniting current should be proportional, if the process is molecular, to the number of molecules of combustible gas in the mixture, or if it is atomic, to the number of atoms of one or more of the constituent elements   From Table IV it will be clear that, as in the continuous current case the igniting current was most nearly proportional to the number of hydrogen atoms in a molecule of the combustible gas, it is here proportional to the total number of atoms in each molecule of combustible gas or in each explosive unit   It follows that the product of the number of molecules of combustible gas in the most inflammable mixture and the number of atoms in each of its molecules should also be constant, and this is seen to be the case in the last column, Table IV.   N is the number of atoms in an explosive unit, N_e the number of atoms in a molecule of combustible gas, p_m the percentage of gas in the most inflammable mixture, and I the lowest point of the curves —

Table IV.

Gas	Formula	Formula weight	Least current, I	p min	N	$I \times p_m$	$\dfrac{I}{N}$	$N \times p_m$	$N_c \times p_m$
Methane	CH_4	16	2 7	10 2	9	27 5	0 30	91 8	51 0
Ethane	C_2H_6	30	4 0	6 9	15	28 3	0 27	103	55 2
Propane	C_3H_8	44	6 45	4 8	21	30 6	0 30	100	52 2
Butane	C_4H_{10}	58	8 8	3 75	27	32 6	0 32	100	51 8
Pentane	C_5H_{12}	72	9 2	3 05	33	26 7	0 28	96	51 8
				Mean values		29 1	294	96 8	52 4

The family of curves in fig 2 for continuous current may be represented by the equation $I = kpn$, where k is the same constant for all the paraffins, p the percentage of gas in any mixture, and n the number of atoms in a molecule of combustible gas   The corresponding equation for the alternating current curves of fig. 12 is $I = aN_c + b(p - p_m)^2$, in which the constant a is the same for all the gases, and b a constant for each gas, increasing with its molecular weight   These equations give the igniting current for any percentage p of combustible gas in air   Methane appears in this to be somewhat out of line with the others   The values of b are, from the curves of fig 12,

	$b.$	b/mol. wt.
Methane　.　.....	0 605	0·0378
Ethane	0 601	0·0200
Propane..	0·909	0·0206
Butane .　　.	1 30	0·0224
Pentane　..........	1 40	0 0194

For the paraffins, therefore, continuous current ignition above the point of perfect combustion varies as the percentage of combustible gas, alternating current ignition as the square of excess of either of the combining gases on each side of the point of maximum inflammability

There can be no doubt that the shape of a molecule must in some way affect its resistance to being broken up, so that great uniformity can scarcely be expected in numerical results of this kind. The methane molecule CH_4 must differ from the higher homologues of the form CH_3-CH_2-CH_2-CH_3, and the results with ethane, propane, and butane agree well together in all cases

The explanation of the difference in type of the benzene and carbon-disulphide ignitions may be that in the latter case there is explosion (without intermediate stages), and that in the former, however ignited, there is first very full dissociation of the molecules around the spark

15 *Cause of Difference between Continuous and Alternating Current Ignition when the Gas Percentage is Varied*

The continuous current curves of figs. 2, 3, 5, and 7 derive their peculiar form from the fact that the igniting current increases in proportion to the number of molecules of combustible gas in unit volume of the mixture The alternating current curves in general are entirely different in shape, and are nearly symmetrical within the limits. The minimum current, either continuous or alternating, must clearly occur at that mixture in which self-ignition is most easily started, and since with continuous current ignition the forcing action of the spark quite masks any changes in the gas in contact with it, it is interesting to examine the conditions most favourable to alternating current ignition The values in Column 5, Table V, are of the percentage of combustible gas ignited by the minimum current

Table V —Ignition by Alternating Currents

	Limits of inflammability		Mean	Observed minimum, from fig 11.	Combustion to CO_2, at per cent	Combustion to CO, at per cent	Mean of two last.
Methane	5 7	14 8	*10 25*	*10 2*	9 5	12 0	*10 7*
Ethane	8 1	10·7	6·90	*6 9*	5 5	7·7	*6 6*
Propane	2 17	7 35	4 76	*4 8*	8·96	6 0	*4 96*
Butane .	1·65	5 7	*8 67*	*8 75*	8·07	4·88	*8 72*
Pentane	1 85	4 5	*2 92*	*8 06*	2 51	8·61	*3·06*

All the paraffin gases are therefore most easily ignited by alternating arcs in mixtures giving combustion neither to CO nor CO_2, but to the

mean of these, and these again agree with the means of the upper and lower limits It would appear from this that the limits of inflammability of the paraffin series, and possibly of others, may be controlled by dilution of the most inflammable mixture symmetrically on either side of combustion intermediate between CO and CO_2 In the case of carbon disulphide and hydrogen there is explosion rather than relatively slow combustion, and the conditions are not the same

Thus while continuous current ignition is easier in mixtures approaching perfect combustion, as shown in Table II, with alternating current an excess of combustible gas favours inflammation, and there is no change of type, but a regular fall and rise of the igniting currents between the limits

16 Alcohol.

The alternating current ignition curves are given in fig 13   They have the same parabolic form as the paraffins, but, unlike them, have the same minimum current, in this resembling the continuous current paraffin curves of fig 2

The limits of inflammability given by Sorel are 2 5 and 8 8 per cent for ethyl alcohol, 4 8 and 20 for methyl alcohol.   Both limits are slightly higher here   The minimum currents occur at 6 3 and 13 per cent , a ratio of 2 06. The ratio of the lower limits of inflammability is 1 9 and of calorific values 1·9   The ratio of the oxygen required for perfect combustion of ethyl to that for methyl alcohol is also 2   It is possible that all the other ratios depend on the oxygen required for complete combination   The ignition is thus more thermal in type than that of any of the other gases examined , alcohol engines might then run to best advantage with a hot spark   The igniting current, at atmospheric pressure and temperature, is about 0 7 of that required for benzene, or of hexane, the chief constituent of petrol

Complete combustion to CO_2 occurs at 12 3 per cent for methyl alcohol, 6 5 per cent. for ethyl alcohol , the most readily ignited mixtures are at 13 and 6·3 per cent. respectively

In the paraffin series the product of the percentage p_m at the minimum of the curve and of the number of atoms of hydrogen in a molecule was constant

This is not the case for the alcohols, as shown in Table VI

The product of p_m and the atoms of oxygen required for perfect combustion is 39 for methyl alcohol, 37·8 for ethyl alcohol

It is probably the oxygen and not the carbon atoms which decide the position of the minimum of the alternating current curves for alcohol ; for both Coquillion and Sorel have observed that the upper limit of inflammability

appears to correspond to the quantity of oxygen capable of burning the hydrogen (Sorel, *loc cit.*).

Table VI

Alcohol	p_m	$p_m \times$ number of atoms in a molecule			$p_m \times N.$
		Carbon	Hydrogen	Total	
Methyl	13 0	*13 0*	52 0	78	117
Ethyl	6 3	*12 6*	37 8	56 ·7	96

17 *Benzene*

With alternating current arcs the most easily ignited mixture is at 4·5 per cent., as seen in fig 4   Combustion to CO_2 is at 2 73 per cent., to carbon monoxide at 4 47 per cent. The curve is symmetrical about the point of combustion *to carbon monoxide alone*   The alternating igniting currents are more than 12 times greater than with continuous voltage The incomplete combustion of benzene in explosion indicated by these results may account for the apparently unavoidable deposit of carbon in engines driven by benzol

18 *Carbon Disulphide.*

This curve (fig 5) is remarkable for its resemblance to the continuous current curve   The least alternating current is about seven times greater than the least continuous igniting current   The limits were not found, but the curve indicates that they are between 1 and 2, and between 40 and 45 per cent.   The ignition of carbon disulphide by alternating current break-sparks is of a more violent or forced character than in most gases.   It should be excellent as a starter of ignition, and this may be its chief *rôle* in commercial benzol for internal combustion engines   It may be well not to attempt to remove it completely in spite of the corrosive action of its products.   The most inflammable mixture is near the point of perfect combustion to CO_2.

19 *Hydrogen and Carbon Monoxide*

The ignition of hydrogen by alternating current break-sparks has several interesting features.   The lower limit is about 10 per cent.   From this the curve (fig 6) falls as if to a minimum at 42 per cent, the point for perfect combustion, and almost midway between the limits usually given of 10 and 72 per cent when ignition is by high tension sparks.   But at 32 per cent. the ignition suddenly changes type, the curve becomes a straight line

passing nearly through the origin and extending to 70 per cent, at which point there is evidence of a more rapid rise of current.

There is here a more than usually clear combination of the alternating and continuous types of ignition

Carbon monoxide, fig. 7, shows a transition between the types, the continuous current curve between the paraffins and hydrogen, the alternating current curve between hydrogen and the symmetrical parabolic curve

20 *Absence of Influence of External Ionisation.*

Although it would appear from the nature of the results that the influence of the arc is confined to a small volume—a few molecules thick perhaps—around it, yet within that space the action must be intense   The effect upon the igniting current of exposing the gas in the explosion vessel to any ionising source such as X-rays or strong ultra-violet light (through quartz windows) is too small to observe when there is no platinum present   It was less than 0·5 per cent. with illuminating gas at atmospheric pressure, which, containing a large proportion of hydrogen, might be expected to be sensitive to ionisation

A glowing static discharge from needle points had also no perceptible influence on ignition.

21 *Summary of Alternating Current Results*

The difference between the continuous and alternating current results arises from the rapidly-reversing electric field across the spark dragging the electrons or ions from pole to pole and preventing their escape into the gas. Alternating igniting currents have therefore to be much greater than continuous currents at the same voltage   This difference is increased by the approach of the period of the current to the time of duration of the break-spark   The latter varies with the voltage in such a manner that the igniting current remains constant in value over a long range of voltage

The igniting currents of the paraffins increase as the order rises, *the product of the minimum current for each gas and the percentage at which it occurs being constant.*

The product of the number of atoms in a molecule of combustible gas and of the above percentage is also constant, *so that the number of atoms in unit volume in all of the most inflammable mixtures is the same.*   The igniting current is most nearly proportional to the number of atoms in the group of one molecule of combustible gas and the oxygen required for combustion forming an explosive unit.   The paraffin gases, after methane, are most easily

ignited at a percentage giving combustion *midway between carbon monoxide and dioxide*, and both limits of inflammability are symmetrical from this point. Benzene is most easily ignited when burning to carbon monoxide, alcohol to carbon dioxide. Carbon disulphide and hydrogen have the forced or continuous current type of ignition   External ionisation which does not itself cause ignition has no measurable influence on the least igniting currents by break-sparks.

22 *Conclusion.*

On the whole it would appear to be probable from the great differences in magnitude and type between continuous and alternating current ignition that some kind of ionisation precedes combustion, for the evidence is strong that a relation between electrification and chemical change not unlike that of ordinary ionisation occurs at ignition, caused possibly by the violent collisions which must occur in the gas in contact with high-temperature sparks.   That a gas has a particular temperature of inflammation may mean that ionisation by collision begins at this temperature—as in the case of ignition by hot wires quoted in §1—with absorption of energy from the source or, later, from that liberated by recombining atoms   On this view, when the molecular energy set free by combustion of a molecule exceeds that required for initial ionisation of an adjoining molecule there is true explosion, and since it is probable that all three modes of molecular motion, translation, rotation, and vibration, have part in the process of ionisation by collision, the influence of temperature, which depends only upon the translational energy, may be in certain cases of secondary importance

The Dispersion of a Light Pulse by a Prism.

By R. A. Houstoun, M.A., Ph.D., D.Sc., Lecturer on Physical Optics in the University of Glasgow

This investigation is a continuation of a former one in which an expression was derived for a light pulse with an energy distribution given by Wien's law.[*] The first three paragraphs are supplementary to the former paper, the rest of the investigation deals with the passage of the same pulse through a prism and its separation into the different colours in the focal plane of a telescope. The general principles according to which this must take place are, of course, known, but here the actual disturbance at every point in the focal plane is given for the first time as a definite function of the time and as a result it is possible to state how many waves there are in the trains, which the single initial pulse gives rise to in the various parts of the spectrum.

§ 1. My general expression for the initial form of a light pulse was

$$\frac{\cos\left(n+\tfrac{1}{2}\right)\theta}{(x^2+h^2)^{(2n+1)/4}},$$

where $\tan\theta = x/h$. I did not notice until after the former paper was communicated, that this expression is

$$\frac{1}{\Gamma(n+\tfrac{1}{2})}\int_0^\infty e^{-h\alpha}\cos\alpha x\,\alpha^{n-\frac12}d\alpha.$$

The pulse is thus equivalent to the superposition of an infinite series of cosine waves of gradually increasing wave-length, the parameter of the wave being connected with the wave-length in air by $\alpha = 2\pi/\lambda$ and the amplitude being given by $e^{-h\alpha}\alpha^{n-\frac12}$. According to the former paper the velocity of such a wave is $1/\sqrt{(\alpha c)}$. Hence after time t the disturbance becomes

$$\frac{1}{\Gamma(n+\tfrac{1}{2})}\int_0^\infty e^{-h\alpha}\cos\alpha\left(x-\frac{t}{\sqrt{(\alpha c)}}\right)\alpha^{n-\frac12}d\alpha.$$

But, when t^2/c was large, the disturbance was shown to be proportional to

$$\frac{t^{2n}}{x^{3n+\frac12}}e^{-t^2h/4cx^2}\cos(t^2/4cx).$$

* "The Mathematical Representation of a Light Pulse," 'Roy. Soc. Proc.,' A, vol. 89, p. 399 (1913)

Consequently on putting in the constants which were neglected formerly for the sake of simplicity we arrive by physical reasoning at the new integral,

$$\left(\frac{t^2}{c}\text{ large}\right)\quad \int_0^\infty e^{-ka}\cos a\left(x-\frac{t}{\sqrt{(ac)}}\right)a^{n-\frac12}da=\frac{\sqrt{\pi}t^{2n}}{4^n c^n x^{2n+\frac12}}e^{-t^2 h/4cx^2}\cos(t^2/4cx).$$

§ 2 Planck's law for black body radiation is

$$\frac{c_1}{\lambda^5}\cdot\frac{1}{e^{c_2/\lambda T}-1}=\frac{c_1}{\lambda^5}\cdot\frac{e^{-c_2/\lambda T}}{1-e^{-c_2/\lambda T}}$$

Except for high temperatures and in the far infra-red, $e^{-c_2/\lambda T}$ is small in comparison with 1   Hence the denominator may be expanded as a series and the law becomes

$$\frac{c_1}{\lambda^5}\left[e^{-c_2/\lambda T}+e^{-2c_2/\lambda T}+e^{-3c_2/\lambda T}+\quad\right].$$

each term being of the form of Wien's law but with the constants multiples of the Wien law constant   It follows, therefore, that the Planck distribution must be given by the initial disturbance formed by superposing the pulses which would give these separate Wien distributions   That is, in the notation of my previous paper, the pulse initially represented by the series

$$\frac{\cos\frac{5}{2}\tan^{-1}(x/h)}{(x^2+h^2)^{5/4}}+\frac{\cos\frac{5}{2}\tan^{-1}(x/2h)}{(x^2+\{2h\}^2)^{5/4}}+\frac{\cos\frac{5}{2}\tan^{-1}(x/3h)}{(x^2+\{3h\}^2)^{5/4}}+$$

gives a distribution of energy obeying Planck's law   This was first pointed out to me by Dr Green

In fig 1 the dotted curve represents the first term of the series and the full curve the sum of the first ten terms of the series both drawn for $h=1$ The addition of the remaining terms of the series would at the most raise the full curve 0 02 all over   There is thus not much difference in the shape of the pulses giving the Wien and Planck distributions

As shown in the former paper h varies inversely as the absolute temperature. If the absolute temperature is doubled, h is halved and it is seen from the form of the curve that the shape of the pulse at the new temperature can be obtained from the first shape by multiplying the ordinates throughout by $2^{5/2}$, i.e. by 5 56, and at the same time moving each of them half way into the centre.   As the temperature increases the pulse thus becomes narrower and sharper   The value $h=1$ corresponds to an absolute temperature of $T=c_2/(4\pi)=1\cdot436/(4\pi)=0\cdot114^\circ$.

The curves representing the successive terms of the series can be obtained from the curve representing the first term by multiplying the ordinates by 0·177, 0·064, 0·031, 0 018, etc., and at the same time moving them out twice, thrice, four times, five times, etc., their distance from the centre.   The full curve in fig. 1 showing the first 10 terms of the series was obtained in this

way by constructing the different terms from the first graphically and then summing then

§ 3 The expressions derived in the previous paper represented plane light pulses moving in the direction of the x axis A little consideration shows that they can easily be adapted to the three-dimensional case of symmetry about a point

Consider the equation

$$\frac{\partial^2}{\partial r^2}(rS) + c^2 \frac{\partial^4}{\partial t^4}(rS) = 0$$

It is solved by $rS = \sin \frac{2\pi}{\tau}\left(t - \frac{r}{v}\right)$, where $v = \pm \tau/(2\pi c)$ S consequently represents a wave diverging from the origin in a medium in which the

Fig 1

Fig 2
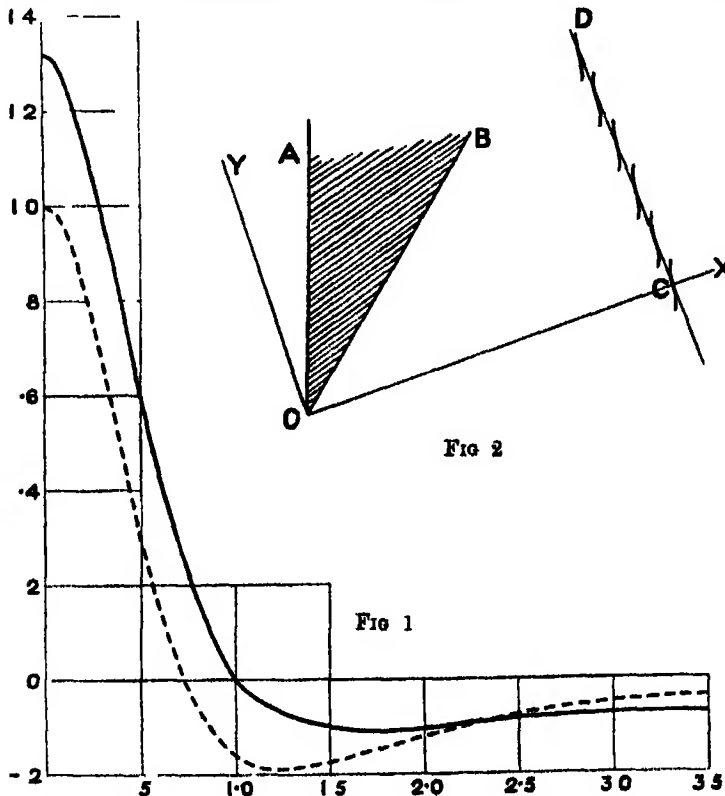
velocity is directly proportional to the period.   By analogy with equation (1) of the former paper

$$rS = \frac{\partial^2}{\partial (vr)^2} \cdot \frac{1}{\sqrt{(h+ir)}} e^{-p^2/4c(h+ir)}$$

is a solution of the above equation. Consequently our former solutions may

be adapted for three-dimensional motion by the simple artifice of writing r for x and multiplying by $1/r$ For example, the initial shape of the disturbance with the Planck distribution of energy is

$$\sum_{n=1}^{n=\infty} \frac{\cos \frac{5}{4} \tan^{-1}(r/nh)}{r(r^2 + \{nh\}^2)^{5/4}}$$

§ 4 Let a plane light pulse with the Wien energy distribution be incident normally on the face OA of the prism AOB (fig 2). Then before incidence it may be represented by

$$\int_0^\infty e^{-h\alpha} \cos \alpha \, (l - vt) \, \alpha^{3/2} d\alpha,$$

where l is distance from OA measured positive from left to right and v is the velocity of light in air   The prism is situated in air and has a refracting angle of 30°   In this section we shall find the shape of the disturbance immediately after passing through the prism   For this purpose we shall ignore the loss by reflection at the faces OA and OB, and shall also assume the prism to be unlimited in the direction OA.

The treatment depends on the principle of the superposition of small vibrations   Let us suppose we have a series of infinitely long trains of cosine waves incident on the prism and that the amplitude of each train is given in terms of its parameter by $e^{-h\alpha}\alpha^{\frac{3}{2}}$ The direction of each train after its emergence from the prism is known, since the index of refraction of the latter is supposed given, and the phase of the emergent wave is also known, since it coincides with the phase of the incident wave at O   Then, since the impulse is equivalent to the superposed cosine trains before incidence, it must be equivalent to them after emergence   It must be observed that in no physical sense are the cosine trains contained in the impulse.

Let OX be the direction of emergence of the cosine train with the greatest amplitude   Denote the parameter of the latter by α_0, then it is easy to show that $\alpha_0 = 3/2\,h$ This train is represented after emergence by

$$e^{-h\alpha_0} \cos \alpha_0 \, (x - vt) \, \alpha_0^{3/2}.$$

The other trains make small angles with OX after emergence and hence must be represented by

$$e^{-h\alpha} \cos \alpha \, (x \cos \theta + y \sin \theta - vt) \, \alpha^{3/2}, \qquad (1)$$

where θ is a function of α Let us assume that $\sin \theta = k\,(1/\alpha_0 - 1/\alpha)$, where k is a constant, this makes the deviation vary with the wave-length in the right direction and gives a function capable of integration. Also assume θ so small that $\cos \theta$ may be put $= 1$ Then after emergence from the prism the total disturbance is given by

$$\int_0^\infty e^{-h\alpha} \cos \alpha \left(x + k\left\{\frac{1}{\alpha_0} - \frac{1}{\alpha}\right\} y - vt\right) \alpha^{3/2} d\alpha$$

$$= \int_0^\infty e^{-h\alpha} \cos \left[\alpha \left\{x + (k/\alpha_0)y - vt\right\} - ky\right] \alpha^{3/2} d\alpha$$

$$= \int_0^\infty e^{-h\alpha} \left[\cos \alpha \left\{x + (k/\alpha_0)y - vt\right\} \cos ky + \sin \alpha \left\{x + (k/\alpha_0)y - vt\right\} \sin ky\right] \alpha^{3/2} d\alpha$$

$$= \frac{\Gamma(\frac{5}{2}) \cos \frac{5}{2} \tan^{-1}[\{x + (k/\alpha_0)y - vt\}/h] \cos ky}{[h^2 + \{x + (k/\alpha_0)y - vt\}^2]^{5/4}}$$

$$\qquad + \frac{\Gamma(\frac{5}{2}) \sin \frac{5}{2} \tan^{-1}[\{x + (k/\alpha_0)y - vt\}/h] \sin ky}{[h^2 + \{x + (k/\alpha_0)y - vt\}^2]^{5/4}}$$

$$= \frac{\Gamma(\frac{5}{2}) \cos [\frac{5}{2} \tan^{-1}(1/h) \{x + (k/\alpha_0)y - vt\} - ky]}{[h^2 + \{x + (k/\alpha_0)y - vt\}^2]^{5/4}}$$

It is evident that after passing through the prism the disturbance is still a pulse and of much the same thickness as before Its characteristics are best studied by giving the constants definite numerical values

Suppose that the temperature of the source is 6000° absolute, the commonly accepted value for the sun   Then

$$h = c_2/4\pi T = 1\,436/24{,}000\pi = 1\,904\ 10^{-5}$$

and $$\alpha_0 = 3/(2 \times 1\,904 \times 10^{-5}) = 7\,87\ 10^4$$

The wave-length corresponding to α_0 is $7\,97\ 10^{-5}$ cm , a value for the extreme red end of the spectrum

If the prism were made of light barium crown glass, the index of refraction for α_0 would be $1\,512$, for $\alpha = 1\cdot066\ 10^5$ (D lines) it would be $1\,517$, for $\alpha = 1\cdot292\ 10^5$ (blue hydrogen line) it would be $1\,523$, and for $\alpha = 1\cdot552 . 10^5$ (violet mercury line) it would be $1\,5318$ The deviations for these wave-lengths would then be respectively 19° 7', 19° 20', 19° 36', and 20° 0'   The differences of the last three figures and the first are 13', 29', and 53'   It is impossible to fix our constant k so as to make the deviations accord exactly with those of any known glass, but if we take $1\,8 . 10^5$ as its value, the excess of the deviations of the last three wave-lengths over the first would be 20', 31', and 38'   We shall take this value for k, thus the dispersive power of the material of our prism is somewhat similar to that of crown glass

Let us now examine the distribution of the disturbance for $t = 10^{-10}$ sec , i.e the time taken by a cosine train to move out 3 cm. from the origin Write $x - vt = \xi$, i.e $\xi = x - 3$ cm   Then, if the constant factor be ignored, the disturbance is the product of

$$\frac{1}{[h^2 + \{\xi + (k/\alpha_0)y\}^2]^{5/4}} \quad \text{and} \quad \cos [\tfrac{5}{2} \tan^{-1}(1/h) \{\xi + (k/\alpha_0)y\} - ky]. \quad (2)$$

The first factor is a maximum along the straight line $\xi + (k/a_0)y = 0$, i.e. $\xi + 0.0229\,y = 0$. This straight line is represented by CD in fig 2. The first factor diminishes to zero on both sides of the maximum and has reached 1/100 of its maximum value at a distance of $\pm 1.19 \times 10^{-4}$ cm. from CD. We shall consider the variation of the second factor only within this distance from CD

As ξ varies from $-\infty$ to $+\infty$, the second factor varies from $\cos\{-(5\pi/4) - ky\}$ to $\cos\{+(5\pi/4) - ky\}$ It cannot thus have more than two maxima for one value of y. The locus of its maxima is given by

$$\tfrac{5}{2}\tan^{-1}(1/h)\{\xi + (k/a_0)y\} - ky = 2n\pi,$$

i.e., $$(1/h)\{\xi + (k/a_0)y\} = \tan\tfrac{2}{5}(2n\pi + ky), \tag{3}$$

which obviously represents a family of curves, one for each value of n. These curves give the position of the crests.

In equation (3) keep $\xi + (k/a_0)y = 0$ and gradually increase y, i.e., move along the straight line CD. Whenever $ky = -2n\pi$, the equation is satisfied, that is, whenever

$$y = -2n\pi/1.8 \times 10^{7}$$

This equation therefore gives the points in which the curves cut CD. They are equidistant and about 3.48×10^{-3} cm. apart.

From (3) we have

$$\frac{d\xi}{dy} + \frac{k}{a_0} = \frac{2hk}{5}\sec^2\tfrac{2}{5}(2n\pi + ky) \tag{4}$$

If we write p to denote the perpendicular distance of the point (ξ, y) from the line CD, then, by (3),

$$\sec^2\tfrac{2}{5}(2n\pi + ky) = 1 + \tan^2\tfrac{2}{5}(2n\pi + ky) = 1 + \frac{p^2}{h^2}.$$

On substituting this in (4) we have

$$\frac{d\xi}{dy} = -\frac{k}{a_0} + \frac{2hk}{5}\left(1 + \frac{p^2}{h^2}\right)$$

All the curves are therefore parallel for a given value of p.

When the first factor has diminished to 1/100 of its maximum value $p^2/h^2 = 39$. On substituting this and the values for h, k and a_0 we find

$$\frac{d\xi}{dy} = -0.0229 + 0.0137 \times 40 = 0.53.$$

For CD itself $d\xi/dy$ has the value -0.0229

From the above results an idea of the position of the crests may be obtained and they are represented in fig 2, very much out of scale, by the short curves crossing CD.

The equation of the crest through C is obtained from (3) by putting $n = 0$ and may be written as

$$p = h \tan \tfrac{1}{2} ky$$

I have drawn it to scale in fig 3. CD denotes the same line as in fig 2 and the lines through G and H parallel to CD are those for which the first factor has 1/100 its maximum value. The ends of the neighbouring crests come into the figure. As has been pointed out, all the crests are equally spaced and have the same shape

It is obvious from fig 2 that the shape of the disturbance is analogous to the ship waves that would be produced by a pressure point moving along OB. This analogy has been used by Dr Green *

An important assumption has been passed over in silence, namely, that $\cos \theta$ may be put $= 1$ in (1). In the violet when $\theta = 38'$, $\cos \theta = 1 - 3.1 \ 10^{-4}$, x is 3 and α is $1.552 \ 10^{5}$. Hence the error introduced in the phase is the large one of 14·4 radians. It diminishes towards the red. It seems, however, from the applications of the principle of stationary phase, that only interference between waves of nearly equal wave-length is important and the relative phase difference of such waves is not affected appreciably by the approximation. In any case the results are rigorous for the neighbourhood of the x axis. If the accurate value is substituted for $\cos \theta$, the expression will not integrate

§ 5. In the previous section the nature of the light was considered immediately after emerging from the prism, before the colours have time to separate out, in the region where, if a screen is interposed, a white rectangular patch is obtained tinged on the one side with red and on the other with violet. We shall now investigate the disturbance in the focal plane of the spectroscope telescope

Hitherto diffraction has been ignored. It is now fundamental. Let the pulse be incident normally on the face OA as before,
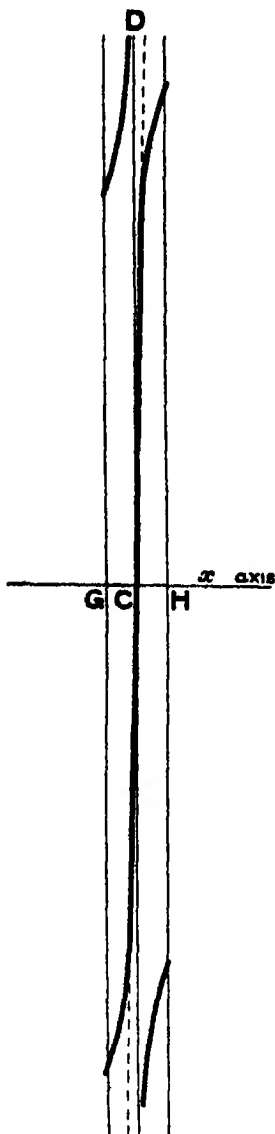
Fig 3

but let there be a screen (fig. 4) on the other face restricting the length OB that can be used   Let b be the greatest thickness of the prism used   After emergence from the prism the light is received by a lens which has the property of making a parallel beam converge to a mathematical point.   The diameter of the lens is so large that it receives all the rays that pass through the aperture OB, the latter causes the diffraction, not the rim of the lens. Reflection and absorption losses are ignored both in the prism and the lens
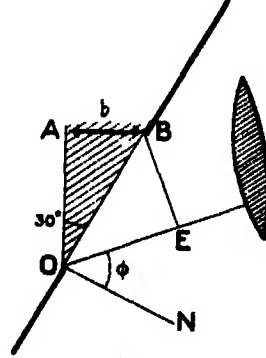
Each point on the face OB must be considered as sending rays of all possible wave-lengths in every direction   Take a definite direction OE, which is specified by the angle ϕ which it makes with ON, the normal to the face OB   To this direction there corresponds a point P in the focal plane of the lens   Let the optical distance of P from O, measured along the ray, be s

Let us consider the disturbance at P due to rays of parameter α We have to sum an infinite number of rays of equal intensity and period but uniformly increasing phase   Let $2p$ be the difference of phase in radian measure between the first and last of them.   Then, as is well known, the amplitude of the resultant varies as $(\sin p)/p$.

If BE is drawn perpendicular to OE and μ denotes the index of refraction of the prism, $OE = OB \sin \phi = 2b \sin \phi$, and consequently

$$2p = \frac{2\pi}{\lambda}(\mu b - 2b \sin \phi) = \alpha b (\mu - 2 \sin \phi)$$

The phase of the resultant is the phase of the mean ray   Consequently the disturbance at P is given by

$$\frac{\sin p}{p} \cos \{\alpha (s - vt) + p\}$$

To get the whole disturbance at P we have to multiply the above expression by $e^{-h\alpha} \alpha^{3/2}$ in order to take account of the shape of the initial pulse, and then integrate with respect to α The result is

$$\int_0^\infty e^{-h\alpha} \frac{\sin p}{p} \cos \{\alpha (s - vt) + p\} \alpha^{3/2} d\alpha,$$

p is of course a function of α.   For the expression to be integrable we are restricted to one function, $g - f\alpha$. We shall assume this value, holding over the question of its justification.   Meantime it should be noted that f and g are constants of the prism and independent of the shape of the incident pulse.

z 2

As we move through the spectrum we know from its physical nature that $(\sin p)/p$ remains zero until we come to one particular point, then rises suddenly to a peak and immediately decreases as suddenly to zero again The other two factors of the cosine in the integrand vary so slowly within this region that they may be taken outside the integral sign. We have left then

$$\int_0^\infty \frac{\sin(g-f\alpha)}{(g-f\alpha)} \cos\{\alpha(s-vt)+g-f\alpha\}\, d\alpha.$$

Write $\alpha - g/f = \beta$ and $g/f = \alpha_1$ Then $\beta = \alpha - \alpha_1$ and the integral becomes

$$\int_{-\alpha_1}^\infty \frac{\sin f\beta}{f\beta} \cos\{\beta(s-vt-f)+\alpha_1(s-vt)\}\, d\beta$$

$$= \int_{-\alpha_1}^\infty \frac{\sin\{\beta(s-vt)+\alpha_1(s-vt)\} - \sin\{\beta(s-vt-2f)+\alpha_1(s-vt)\}}{2f\beta}\, d\beta$$

$$= \int_{-\alpha_1}^\infty \frac{\sin\beta(s-vt)\cos\alpha_1(s-vt) + \sin\alpha_1(s-vt)\cos\beta(s-vt)}{2f\beta} - \qquad . \, d\beta$$

$$= \cos\alpha_1(s-vt)\int_{-\alpha_1}^\infty \frac{\sin\beta(s-vt) - \sin\beta(s-vt-2f)}{2f\beta}\, d\beta$$

$$\qquad + \sin\alpha_1(s-vt)\int_{-\alpha_1}^\infty \frac{\cos\beta(s-vt) - \cos\beta(s-vt-2f)}{2f\beta}\, d\beta$$

$$= \frac{1}{2f}\cos\alpha_1(s-vt)\left[\int_{-\alpha_1(s-vt)}^{\infty(s-vt)} \frac{\sin y}{y}\, dy - \int_{-\alpha_1(s-vt-2f)}^{\infty(s-vt-2f)} \frac{\sin y}{y}\, dy\right]$$

$$\qquad + \frac{1}{2f}\sin\alpha_1(s-vt)\left[\int_{-\alpha_1(s-vt)}^{\infty(s-vt)} \frac{\cos y}{y}\, dy - \int_{-\alpha_1(s-vt-2f)}^{\infty(s-vt-2f)} \frac{\cos y}{y}\, dy\right] \qquad (5)$$

The integrals in the brackets are known as the sine integral and cosine integral, and their values have been calculated for all values of y by J. W. L. Glaisher.[*]

The first bracket can be re-written

$$\int_{-\alpha_1(s-vt)}^{-\alpha_1(s-vt-2f)} \frac{\sin y}{y}\, dy + \int_{\infty(s-vt-2f)}^{\infty(s-vt)} \frac{\sin y}{y}\, dy.$$

Let us consider the second term first. It will be shown farther down that $2f$ is positive and much smaller than s When $t = 0$ both limits are $+\infty$, when $t = (s-2f)/v$ the lower limit changes to $-\infty$, and when $t = s/v$ the upper limit changes to $-\infty$. The value of the integral between the limits $\pm\infty$ is, of course, π. Hence from $t = (s-2f)/v$ to $t = s/v$ the integral is π; before and after this it equals zero

Next consider the other term. When $t = 0$ it is zero. As t approaches $(s-2f)/v$ it suddenly approaches $\tfrac{1}{2}\pi$ then as the upper limit changes

* 'Phil. Trans,' vol 160, pp. 367–387 (1870).

sign and becomes positive, it increases to π It will be shown farther down that the upper limit practically reaches $+\infty$ long before the lower limit changes sign   As the lower limit becomes zero and then positive the integral decreases again to zero   The changes are the same as for the second term, only they take place continuously

The second bracket can be written

$$\int_{-a_1(s-vt)}^{-a_1(s-vt-2f)} \frac{\cos y}{y} dy + \int_{\infty(s-vt-2f)}^{\infty(s-vt)} \frac{\cos y}{y} dy,$$

but this integral, though very great near the origin, diminishes rapidly to a small quantity, is zero at infinity, and so can be neglected in comparison with the other one

Our final result, therefore, for the disturbance at P, when the term left outside the integral sign is included, is

$$\frac{\pi}{f} e^{-ha_1} a_1^{3/2} \cos a_1 (s-vt) \tag{6}$$

between the times $t = (s-2f)/v$ and $t = s/v$ Outside these limits there is no disturbance

We had
$$p = ab\left(\frac{\mu}{2} - \sin\phi\right) = g - fa,$$

hence
$$\frac{\mu}{2} = \sin\phi - \frac{f}{b} + \frac{g}{ba} . \tag{7}$$

This gives
$$\frac{d\mu}{d\lambda} = \frac{g}{\pi b}$$

The dispersion is therefore uniform throughout the spectrum   Unfortunately it runs the wrong way, μ increases with λ.   Let us suppose that $b = 2$ cm. and that $d\mu/d\lambda$ is 500, which is about the value for crown glass in the neighbourhood of the D lines   Then $g = 1000\pi$ If a_1 has the value for the D lines, 1 066 10^5, $f = g/a_1 = 0\ 0293$, and $2fa_1 = 6\ 28\ .\ 10^3$ As the sine integral for $y = 75$ differs only by 1 per cent. from its value for infinity, the assumption made above is justified   It will be observed that it is not necessary to fix the value of μ, though from equation (7) it cannot be greater than 2 for the wave-length in question.

The number of complete wave-lengths in the train is $2f/\lambda = a_1 f/\pi = g/\pi = b\frac{d\mu}{d\lambda}$, Rayleigh's expression for the resolving power   Its numerical value in this case is 1000.

It should be noted that the expression giving p in terms of a is always of the same form.   For let ϕ have the value ϕ'.   Then

$$p = ab\left(\frac{\mu}{2} - \sin\phi'\right),$$

which gives, on substituting from (7) for $\mu/2$,

$$p = ab\left(\sin\phi - \frac{f}{b} + \frac{g}{ba} - \sin\phi'\right)$$

$$= g - a\left(f + b\{\sin\phi' - \sin\phi\}\right),$$

which can be written $g - af'$. The value of g thus remains the same, but the value of f changes with ϕ

We have $\qquad\qquad f' = f + b\{\sin\phi' - \sin\phi\},$

which, on proceeding to the limit, gives

$$df = b\cos\phi\, d\phi$$

But $f = g/a$, hence $df = -(g/a^2)\, da$, and consequently

$$g\, da = -a^2 b \cos\phi\, d\phi \qquad\qquad (8)$$

§ 6 Let us now verify the analysis of the preceding section by integrating the energy in the different parts of the spectrum and comparing the result with the energy in the initial pulse

The latter can be represented by

$$\int_{-\infty}^{+\infty} dx \left(\int_0^\infty e^{-ha}\cos ax\, a^{3/2} da\right)^2 = \int_{-\infty}^{+\infty}\left\{\frac{\Gamma(\tfrac{5}{2})\cos\tfrac{5}{2}\tan^{-1}(x/h)}{(x^2 + h^2)^{5/4}}\right\}^2 dx,$$

which, by the preceding paper, is equal to

$$\frac{2}{h^4}\{\Gamma(\tfrac{5}{2})\}^2 \int_0^{\pi/2} \cos^2\frac{5\theta}{2}\cos^4\theta\, d\theta$$

Now $\qquad \displaystyle\int_0^{\pi/2}\cos^2\frac{5\theta}{2}\cos^3\theta\, d\theta = \tfrac{1}{8}\int_0^{\pi/2}(1 + \cos 5\theta)(\cos 3\theta + 3\cos\theta)\, d\theta$

$$= \tfrac{1}{8}\int_0^{\pi/2}(\cos 3\theta + 3\cos\theta + \tfrac{1}{2}\{\cos 8\theta + \cos 2\theta\} + \tfrac{3}{2}\{\cos 6\theta + \cos 4\theta\})\, d\theta$$

$$= \tfrac{1}{8}(-\tfrac{1}{3} + 3) = \tfrac{1}{3}$$

and $\qquad\qquad \Gamma(\tfrac{5}{2}) = (\tfrac{3}{4})\cdot\dfrac{\sqrt{\pi}}{2},$

hence the incident energy can be represented by

$$\frac{3\pi}{8h^4} \qquad\qquad (9)$$

Before proceeding to find the energy in the spectrum an additional factor must be added to (6). It was stated that the amplitude of the wave diffracted in the direction ϕ was proportional to $(\sin p)/p$ We are now concerned with absolute values, and must determine the constant of proportionality, which for the sake of simplicity was previously omitted.

If a harmonic wave is incident normally on the prism, on emerging it is

diffracted in a number of different directions which are grouped symmetrically about the direction given by $p = 0$ The energy in the range comprised between ϕ and $\phi + d\phi$ is proportional to $\{(\sin p)/p\}^2 d\phi$. Now $p = ab(\mu/2 - \sin \phi)$, hence since we are here confined to one wave-length $dp = ab \cos \phi \, d\phi$ The energy in this range is therefore proportional to

$$\left(\frac{\sin p}{p}\right)^2 \cdot \frac{dp}{ab \cos \phi}$$

The energy in the incident wave has been taken implicitly as 1, hence, if we integrate the above expression over all values of p, divide the result into 1 and take the square root, we shall find the desired constant The result is

$$\sqrt{\left(\frac{ab \cos \phi}{\pi}\right)}$$

The more accurate expression to be used instead of (6) is therefore, on omitting the suffixes,

$$\frac{\pi}{f} \sqrt{\left(\frac{ab \cos \phi}{\pi}\right)} e^{-h_a \alpha^{1/2}} \cos \alpha (s - vt) \tag{10}$$

To measure the energy in this wave take the mean square of the amplitude and multiply by the length of the train, $2f$. The result is

$$\frac{1}{2} \left(\frac{\pi ab \cos \phi}{f^2} e^{-2h_a \alpha^3}\right) 2f$$

This as yet represents only the energy in a single direction and is of course infinitely small. To find the energy in the whole spectrum we must multiply by $d\phi$ and integrate over all possible values of ϕ This is done by evaluating $d\phi$ in terms of $d\alpha$ by means of (8) The result is then

$$-\pi \int_0^\infty e^{-2h_a \alpha^3} d\alpha = \frac{3 \pi}{8 h^4},$$

which agrees perfectly with (9)

§ 7. To show how the amplitude varies at the beginning of the train I have drawn up the following table. The first, fourth, and seventh columns

−6·28	+0 14	−0·030			+0·628	+5 30	−0·014
−5·65	+0 12	−0·110			+1 25	+5 84	−0 43
−5·02	+0·05	−0 188			+1 89	+6·24	−0·44
−4 39	−0 10	−0 187			+2·52	+6 49	−0 28
−3 76	−0 23	−0·095	0·000	+4 69	+3 13	+6 54	+0·076
−3 13	−0 23	−0·076			+3·76	+6 49	+0·095
−2 52	−0 21	+0 28			+4 39	+6 36	+0 187
−1·89	+0 02	+0 44			+5·02	+6·21	+0 188
−1 25	+0 42	+0·43			+5·65	+6·14	+0 110
−0·628	+0·96	+0 014			+6·28	+6 12	+0·030

give the phase in radians measured from the time $t = (s - 2f)/v$; it increases in steps of $\pi/5$. The figures with the minus sign denote time before the arrival of the wave proper. The second, fifth, and eighth columns give the value of the first square bracket in (5), and the third, sixth, and ninth columns the value of the second square bracket.

The table shows that 97 per cent of the growth of the amplitude takes place within two wave-lengths and, as mentioned above, there are 1000 wave-lengths in the train It thus starts very suddenly. The infinite amplitude in the second column does not seem to influence the total energy appreciably as it was neglected in § 6

At the end of the train the changes are gone through in the reverse order, and in addition the sign of the infinite amplitude is changed

§ 8. It is obvious that the results in § 5 do not depend on the shape of the prism or on the fact that the pulse is incident perpendicularly Also, although derived for one particular law of dispersion, they hold for any law of dispersion. The $(\sin p)/p$ term varies so rapidly with μ that $d\mu/d\lambda$ can be taken as constant within the range of integration. Now f was shown to equal $(b\lambda/2)\, d\mu/d\lambda$. Hence the results may be made independent of our particular law of dispersion by the substitution of this value for f

§ 9 Hitherto the incident disturbance has been a pulse Let us now suppose it to be a limited harmonic wave, that it is represented by

$$\cos \beta (x - vt),$$

but that the wave starts suddenly, continues for N complete wave-lengths and then stops suddenly. To find the effect of the prism on this train it is necessary first to reverse the ordinary procedure and, instead of analysing a pulse into waves, analyse the wave into pulses. Suppose the wave built up of a number of rectangular pulses, all of the same base length but having different heights. Then each of these pulses is dispersed by the prism into a system of wave trains , the wave trains for the different pulses differ among themselves in amplitude and phase If we fix our attention on the point in the spectrum specified by α, in the limit when the pulses are made infinitely thin, the superposition of the wave trains gives at this point

$$\int \cos \beta vt_0 \cos \alpha (x - v\{t - t_0\})\, dt_0. \tag{11}$$

$= t_0$ gives the time at which the elementary pulse reaches the prism and $\cos \beta vt_0$ its height.

Let the resolving power at the wave-length in question be R, and let $2\pi R/\alpha$, the length of the train into which a pulse is dispersed, be greater

than $2\pi N/\beta$, the whole length of the incident train   Then for a length $2\pi(R/\alpha - N/\beta)$ all the wave trains overlap completely, on each side of this there is a length $2\pi N/\beta$, in which the overlapping takes place echelon-wise, at one end of which we have only a single train due to the first or last elementary pulse of the original train and, as we progress through which, the trains due to the other elementary pulses are gradually added, until at the other end we have all the trains due to the initial wave. For the middle region the integral (11) is to be taken over a range $2\pi N/(\beta v)$, for the end regions, as we move outwards from the middle, the range gradually diminishes from this value to zero

Let us suppose that $\beta \neq \alpha$, then

$$\int \cos\beta\, vt_0 \cos\alpha\, (x - v\,\{t - t_0\})\, dt_0 = -\frac{1}{2(\alpha+\beta)v} \sin\{\alpha(x-vt) + vt_0(\alpha+\beta)\}$$
$$-\frac{1}{2(\alpha-\beta)v} \sin\{\alpha(x-vt) + vt_0(\alpha-\beta)\}$$

If $\alpha = \beta$ the integral becomes

$$-\frac{1}{4\beta v}\sin\{\beta(x-vt) + 2\beta vt_0\} + \frac{t_0}{2}\cos\beta(x-vt)$$

When the limits are substituted, it is obvious that it is only the second term of the second case that becomes important   Within the middle region it has a value

$$\frac{\pi N}{\beta v}\cos\beta(x-vt),$$

in the end regions the amplitude diminishes uniformly from $\pi N/(\beta v)$ to zero.

As was to be expected, therefore, the limited harmonic train has been refracted to one particular point in the spectrum   There it produces a train with $N+R$ waves, during the first N of which the amplitude steadily increases, for the next $R-N$ of which it is constant and for the last N of which it decreases.   In the train there are no irregular changes of phase.

But when $\beta \neq \alpha$ the integral does not vanish   Consequently the other regions of the spectrum are not absolutely dark   With a bright line spectrum there must thus always be associated a faint background due simply to the fact that the harmonic trains producing the bright lines are limited   Theoretically it should be possible from a comparison of the intensities of the line and background to obtain a lower limit to the number of periods in the initial train.

§ 10. Let us suppose that instead of a limited harmonic train N equal pulses fall on the prism, one after the other, and that the time interval

between the incidence of successive pulses is always the same and equal to t_0. Then the integral (11) gives place to a summation, namely,

$$\cos \alpha (x - vt) + \cos \alpha (x - v \{t - t_0\}) + \quad + \cos \alpha (x - v \{t - (N-1)t_0\})$$
$$= \frac{\cos \{\alpha (x - vt) + \frac{1}{2}(N-1) \alpha vt_0\} \sin \frac{1}{2}(N \alpha vt_0)}{\sin \frac{1}{2}(\alpha vt_0)}$$

The result may be regarded as a wave with a variable amplitude   The amplitude has a maximum equal to N, when $\alpha vt_0 = 2n\pi$, n being any integer   Now $\alpha = (2n\pi)/(vt_0)$ gives an infinite number of points in the spectrum   The train of pulses has thus given rise to something like a spectral series, the convergence frequency is, of course, away at the extreme end of the spectrum at wave-length zero.   The lines of the series are quite as sharp as the maximum of a diffraction grating with N rulings, the expressions for the variation of the intensity being exactly the same in the two cases

Modern investigation has shown spectra to be extraordinarily complicated How far is it possible to introduce simplicity by ascribing different lines to the same common train of pulses, pulses delivered according to laws yet to be discovered, not necessarily at equal time intervals as in this case ?

On Protection from Lightning and the Range of Protection afforded by Lightning Rods *

By Sir Joseph Larmor, F R S, and J. S. B Larmor, M A

The elasticity of the æther is perfect, and a perfect vacuum is infinitely strong, so that no electric force, however great, can produce disruptive discharge through it   The electric weakness of a rarefied gas is now known to be connected (J S Townsend, J J Thomson) with the long free paths of whatever ions may exist in it ; their length allows time for the ions to attain abnormally high velocities, under the acceleration produced by the forces of an electric field, before they are deflected by collisions, and thus enables them to produce more ions in geometrical progression, by shattering impact as they come into collision with the molecules of the gas.

At ordinary densities, with their short free paths, it requires much stronger fields to get up the velocities requisite to induce such an explosively increasing

accumulation of ions   In free space, away from disturbing solid walls, each gas, in fact, is recognised to have definite electric strengths corresponding mainly to the different values of its density

In the strong fields generated by atmospheric accumulations of electricity, we can thus conceive that, owing to displacements of the charged masses by wind and their mutual attractions, the limit of strength is reached at some point of most intense force.   We can think of a small region surrounding that point as breaking down, so that positive ions are drawn away from its interior, and accumulated towards its boundary following the direction of the line of force, the conjugate negative ions accumulating on the boundary in the opposite direction   These aggregations constitute an electric polarity of this labile region, which disturbs the surrounding field that produced them, intensifying it along the line of force (three times for the case of a sphere) and reducing it in sideways directions   Thus the disruption, which there began, will tend to spread along the line of force both forward and backward   The electric discharge is therefore a rupture of the gas *along a line*, not along a surface like rupture of a solid body due to disruptive waves or elastic over-strain , and the line of rupture tends to spread in both directions along the line of electric force which passes through that point of maximum force at which the discharge originated   It might be asked whether this tendency would be modified by the electric force induced kinetically by the discharge , but that also is in the same general direction as the other part

When it is borne in mind that discharge is due to electric rupture of the gaseous medium, which is propagated in time, the question of the direction in which a discharge strikes acquires a meaning   The initial rupture is to be expected at a place of maximum force , and it spreads in both directions, though with different characteristics, along the line of force.   For example, in the case of a lightning rod the discharge would start at the summit of the rod, which is the place of most intense strain, and strike away from the rod instead of towards it

The zigzag character of many discharges also becomes more directly interpretable   For discharge from one cloud mass to another alters the charge in each, and so alters profoundly the fields of force between them and other adjacent masses, thus inciting immediate new discharges between those bodies.   Something of this kind is perhaps indicated by the discontinuous crackle of a sharp discharge.   It is hardly necessary to mention that the duration of thunder, so far as it is not of the nature of reverberation by reflexion, is due to the longer time that the sound takes to arrive from the more distant parts of the flash, and thus gives a sort of analysis of its progress

When once an ionised path has been opened up in the gas there will be

a strong tendency for subsequent discharges to take place along it.   Meantime the line of ionised gases, forming the open path, will be blown into a new position by the wind, and this may not inconceivably have something to do with the origin of the frequently photographed parallel flashes

Such considerations, as regards the propagation of disruptive discharge, may have also to do with the establishment of the beautiful brush discharges which are propagated into the gas, and are of different types for positive and negative ions   The branching character of a sharp negative spark suggests obstacles to the natural direction of travel along the line of force, the positive discharge, being conditioned by different and perhaps more massive ions, will be of more sluggish type   The nature of the gas is known to affect the exquisite patterns made by discharge along photographic plates

Considerations like the above suggest that we may estimate the region of protection of a lightning rod, by inspection of a diagram of the modification of the field of force which is established around the rod, before discharge, owing to its influence   We can render the problem definite by supposing that a single vertical rod or column connected to a horizontal earth is situated in an atmospheric field of vertical electric force of uniform intensity A discharge striking into the modified field surrounding the structure will tend to follow the lines of force, except so far as its initial electric momentum delays that tendency, and, to an extent to be now determined, it will be guided to the upper part of the structure instead of striking downward to the earth as it would do in the absence of that conductor

This special form of the problem of determining a disturbed field of force has a ready solution for the case of a semi-ellipsoidal conductor (a, b, c) standing on the ground, and a rod (of suitably varying section) may be illustrated by the special case in which the semi-axes a and b are small, while c is large.   In fact, if the undisturbed vertical atmospheric field is F, the modified potential

$$V = -Fz + Az \int_z^\infty \frac{d\lambda}{(a^2+\lambda)^{\frac{3}{2}}(b^2+\lambda)^{\frac{3}{2}}(c^2+\lambda)^{\frac{1}{2}}}$$

will be null over the ground, and also null over the ellipsoid (a, b, c), provided

$$\frac{F}{A} = \int_0^\infty \frac{d\lambda}{(a^2+\lambda)^{\frac{3}{2}}(b^2+\lambda)^{\frac{3}{2}}(c^2+\lambda)^{\frac{1}{2}}}.$$

For our special case of a thin symmetrical semi-ellipsoid of height c, this gives

$$V = -Fz + Az \int_z^\infty \frac{d\lambda}{\lambda(c^2+\lambda)^{\frac{1}{2}}}.$$

The value of this integral, however, increases indefinitely towards its lower limit as e falls to zero, when a and b are null   Thus as the semi-ellipsoid becomes thinner the value of A diminishes without limit   that is, the modification of the field of force by a very thin rod is negligible along its sides unless close to it.   A thin isolated rod thus draws the discharge hardly at all unless in the region around its summit

Our special problem is, in fact, the same as if the earth were abolished, and we had to examine the influence of the presence of a complete ellipsoidal conductor, uncharged, on a uniform field of force, in this case parallel to its longest axis.   As the ellipsoid (or solid of other form) becomes very thin, the moment of the charge induced on it, depending as it does on considerations of volume, becomes negligible, the actual value for any rod depending on the form and mode of variation of the cross-section , *cf.* Green's problem of the magnetisation induced in an iron cylinder* in a uniform magnetic field, treated in his Essay, and referred to in Maxwell, 'Electricity and Magnetism,' vol 2, § 439

We are to take it, then, as a general principle, that it is the building to which the lightning rod is attached that modifies the electric field, and so draws the discharge, by virtue of its conducting materials and on account of its breadth being substantial compared with its height *   The structure protects the region around its base, by directing discharge to its own upper parts, which therefore need protection by conductors adequate to draw off this discharge to earth , and vertical rods, joining together if need be lower down, but rising from the corners of the structure to a height which need not be more than about half its breadth, will lift up the field of concentrated electric force from the region directly above the building to the region above their summits, and thus will themselves take the discharge instead of the upper part of the structure.   It would thus appear to be the top of a building that needs protection by rods of some height studded over it, and in direct easy connection with earth.   For convenience and security of communication the rods may rise from a network spread over the roof, but the essential feature appears to be their lifting the field of intenser force to the region in which their free ends are immersed

This mode of analysis can be illustrated more widely by the diagram annexed of the lines of force belonging to a semi-ellipsoid of finite breadth

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* Mr S. G. Brown informs us that instances of damage of radiotelegraphic stations by lightning have occurred, and it has been the subject of remark that the discharge does not come down the antennæ   On the other hand, conducting stay-wires tend to transfer an antenna from the character of a pole to that of a cone   the mast of a ship may come under this case

standing on the ground   For the influence of a semi-ellipsoidal conducting structure on the field is the same as the influence of a larger confocal semi-ellipsoid on a field less intense by a factor which can be readily estimated   In this way, by combining the same ellipsoidal field with uniform exciting fields of various intensities, we can realise a wide range of cases

The mode in which a uniform vertical field will be fenced off from a structure by an arrangement of projecting rods may be illustrated by Plate 11 in Maxwell's 'Electricity and Magnetism,' vol 1, which represents the protection afforded by a series of parallel plates running inward from the left of the page, the lines of equal potential being the vertical curves.   The field of force is promptly annulled, being reduced to half its intensity before it penetrates within the points to a quarter of the distance between adjacent ones.

It is easy to see that a lightning rod is most effective when it lies along the lines of force   If it is at right angles to them it is hardly effective at all It is commonly held that a powder magazine would be best protected if it were enclosed in a network of rods   The horizontal rods would be of use, however, only when the electric discharge is oblique.   If we could assume that the lines of force in a storm are always vertical, a system of vertical rods would serve as well as a network.

When a discharge has once become established, by the opening up of an ionised conducting path, a lightning rod can do little to deflect its course What it can do, and still better a series of rods rising over the whole structure can do, is to provide the easiest and therefore most probable path for such discharge as may be attracted by the structure.   It seems open to question whether merely encasing a building in a wire network will always protect it from a disruptive discharge striking down upon it, unless the network is so fine as to approximate to a complete metallic covering, a spread of connected metallic points some height above the building would appear to be more effective, and might even by themselves suffice to take up and guide away any likely stroke

The considerations above set out have rested on the hypothesis that there is no discharge from the rod into the surrounding field.   But if it is sharply pointed, the very intense field set up close to the point establishes a quiet discharge of ions which, so far as they are not blown away, will form a conducting region around the point, in which the field is relieved   The influence of the rod is then to be likened to that of a conducting globe at its summit, connected to earth by a thin wire   Accordingly, it is of some interest to exhibit the modification which is thus imposed on a uniform
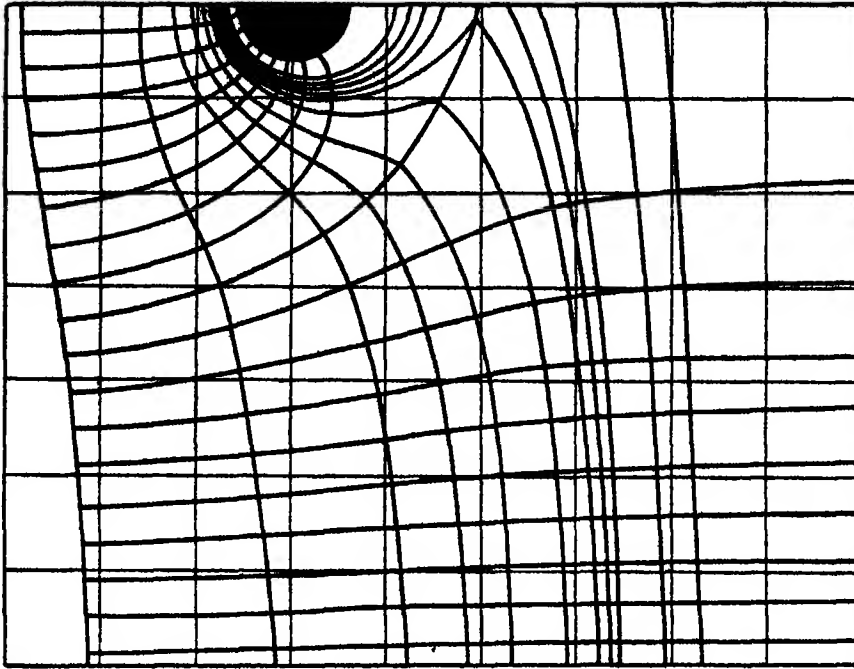
DIAGRAM 2.—Vertical Field of Force disturbed by Globe connected to Earth.
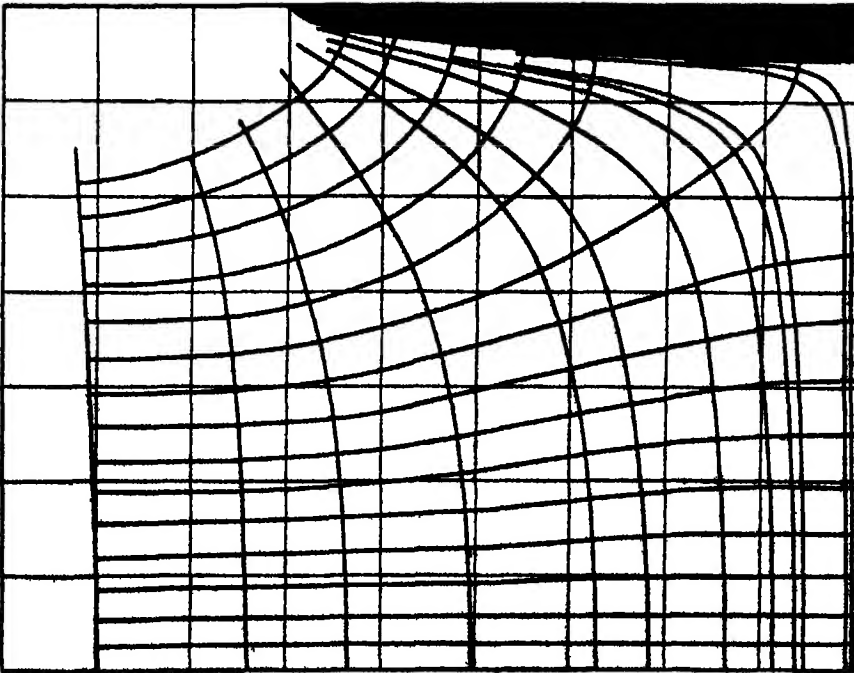
DIAGRAM 1.—Vertical Field of Force disturbed by Semi-ellipsoidal Column.

vertical field of force, F, say, by a globe of radius a with its centre at height c and earthed The globe acquires such a charge e as reduces its potential to zero thus $-Fc + e/a$ must vanish, so that its charge is Fca, the potential of the field therefore becomes

$$V = -Fz + Fca\left(\frac{1}{r_1} - \frac{1}{r_2}\right),$$

where r_1, r_2 represent distances from the centres of the globe and its image If the lines of equal potential which pass underneath the globe are continued down the length of the rod to meet those coming in from the side, the circumstances of the rod with conducting region at its summit will be roughly represented

The diagram 1 represents a uniform field with vertical lines of force and horizontal equipotential lines overhead, as disturbed by a thin conductor of the form of a semi-ellipsoid standing on the ground, the left-hand half of the field is drawn

The diagram 2 represents a similar field overhead disturbed by the presence of a conducting sphere connected to earth by an infinitely thin wire

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Some Calculations in Illustration of Fourier's Theorem.

By Lord Rayleigh, O M., F R S.

According to Fourier's theorem a curve whose ordinate is arbitrary over the whole range of abscissæ from $x = -\infty$ to $x = +\infty$ can be compounded of harmonic curves of various wave-lengths. If the original curve contain a discontinuity, infinitely small wave-lengths must be included, but if the discontinuity be eased off, infinitely small wave-lengths may not be necessary. In order to illustrate this question I commenced several years ago calculations relating to a very simple case. These I have recently resumed, and although the results include no novelty of principle they may be worth putting upon record.

The case is that where the ordinate is constant (π) between the limits ± 1 for x and outside those limits vanishes.

In general

$$\phi(x) = \frac{1}{\pi}\int_0^\infty dk \int_{-\infty}^{+\infty} dv\, \phi(v) \cos k(v-x). \tag{1}$$

Here

$$\int_{-\infty}^{+\infty} dv\, \phi\,(v)\cos k\,(v-x) = 2\pi \cos kx \int_0^1 dv \cos kv = 2\pi \cos kx\,\frac{\sin k}{k}$$

$$= \frac{\pi}{k}\left\{\sin k\,(x+1)-\sin k\,(x-1)\right\},$$

and

$$\phi\,(x) = \int_0^\infty \frac{dk}{k}\left\{\sin k\,(x+1)-\sin k\,(x-1)\right\} \qquad (2)$$

As is well known, each of the integrals in (2) is equal to $\pm\frac{1}{2}\pi$, so that, as was required, $\phi\,(x)$ vanishes outside the limits ± 1 and between those limits takes the value π It is proposed to consider what values are assumed by $\phi(x)$ when in (2) we omit that part of the range of integration in which k exceeds a finite value k_1

The integrals in (2) are at once expressible by what is called the *sine-integral* defined by

$$Si\,(\theta) = \int_0^\theta \frac{\sin\theta}{\theta}\,d\theta \qquad (3)$$

Thus

$$\phi\,(x) = Si\,k_1\,(x+1)-Si\,k_1\,(x-1), \qquad (4)$$

and if the sine-integral were thoroughly known there would be scarcely anything more to do.   For moderate values of θ the integral may be calculated from an ascending series which is always convergent   For larger values this series becomes useless, we may then fall back upon a descending series of the semi-convergent class, viz,

$$Si\,(\theta) = \frac{\pi}{2}-\cos\theta\left\{\frac{1}{\theta}-\frac{1\ 2}{\theta^3}+\frac{1\ 2\ 3\ 4}{\theta^5}-\quad\right\}$$

$$-\sin\theta\left\{\frac{1}{\theta^2}-\frac{1\ 2\ 3}{\theta^4}+\frac{1\ 2\ 3\ 4\ 5}{\theta^6}-\quad.\right\}. \qquad (5)$$

Dr. Glaisher[*] has given very complete tables extending from $\theta = 0$ to $\theta = 1$, and also from 1 to 5 at intervals of 0 1.   Beyond this point he gives the function for integer values of θ from 5 to 15 inclusive, and afterwards only at intervals of 5 for 20, 25, 30, 35, etc   For my purpose these do not suffice, and I have calculated from (5) the values for the missing integers up to $\theta = 60$.   The results are recorded in the Table on p. 320.   In each case, except those quoted from Glaisher, the last figure is subject to a small error

For the further calculation, involving merely subtractions, I have selected the special cases $k_1 = 1, 2, 10$.   For $k_1 = 1$, we have

$$\phi\,(x) = Si\,(x+1)-Si\,(x-1). \qquad (6)$$

[*] 'Phil. Trans.,' vol. 160, p. 367 (1870).

θ.	Si(θ)	θ	Si(θ)	θ.	Si(θ)	θ	Si(θ).
16	1·63130	28	1 60474	39	1 56384	50	1 55162
17	1 59018	29	1 59731	40	1 58699	51	1 55600
18	1 53662	30	1 56676	41	1 59494	52	1 57357
19	1 51868	31	1·54177	42	1 58063	53	1·58798
20	1 54824	32	1·54424	43	1 55836	54	1 58684
21	1 59490	33	1 57028	44	1 54806	55	1 57072
22	1·61609	34	1 59525	45	1 55871	56	1 55574
23	1·59546	35	1 59692	46	1 57976	57	1 55490
24	1 55474	36	1 57512	47	1 59184	58	1 56845
25	1·53148	37	1·54861	48	1 58445	59	1 58368
26	1 54467	38	1 54549	49	1 56507	60	1 58675
27	1 58029						

In every case $\phi(x)$ is an even function, so that it suffices to consider x positive.

$$k_1 = 1.$$

x.	φ(x)	x	φ(x)	x	φ(x).
0·0	+1 8922	2 5	+0 5084	6 0	−0 0958
0 5	1·8178	3 0	+0 1528	7 0	+0 1495
1 0	1 6054	3 5	−0·1244	8 0	+0·2104
1 5	1 2854	4·0	−0·2987	9 0	+0·0642
2 0	0·9026	5·0	−0 3385	10 0	−0 0867

$X_1 = 1$
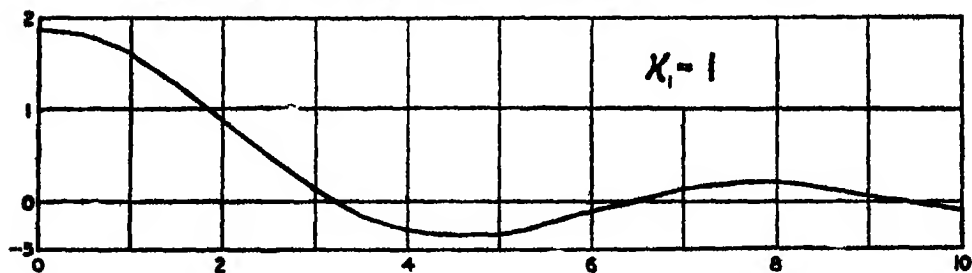
When $k_1 = 2$, $\qquad \phi(x) = \mathrm{Si}(2x+2) - \mathrm{Si}(2x-2),$ $\qquad\qquad$ (7)

and we find

$$k_1 = 2.$$

x.	φ(x).	x	φ(x).	x.	φ(x)
0 0	+3·2106	0·9	+1·9929	3·0	−0 1840
0·1	3 1934	1 0	1·7582	3·5	+0·1151
0·2	3 1417	1 1	1·5188	4·0	+0·2337
0 3	3 0566	1 2	1·2794	4·5	+0·1237
0·4	2 9401	1 3	1·0448	5·0	−0·0692
0 5	2·7947	1 4	0·8179	5·5	−0·1657
0 6	2 6235	1·5	+0 6068	6 0	−0·1021
0 7	2·4300	2·0	−0·1807		
0 8	2 2184	2 5	−0·3940		

Both for $k_1 = 1$ and for $k_1 = 2$ all that is required for the above values of $\phi(x)$ is given in Glaisher's tables
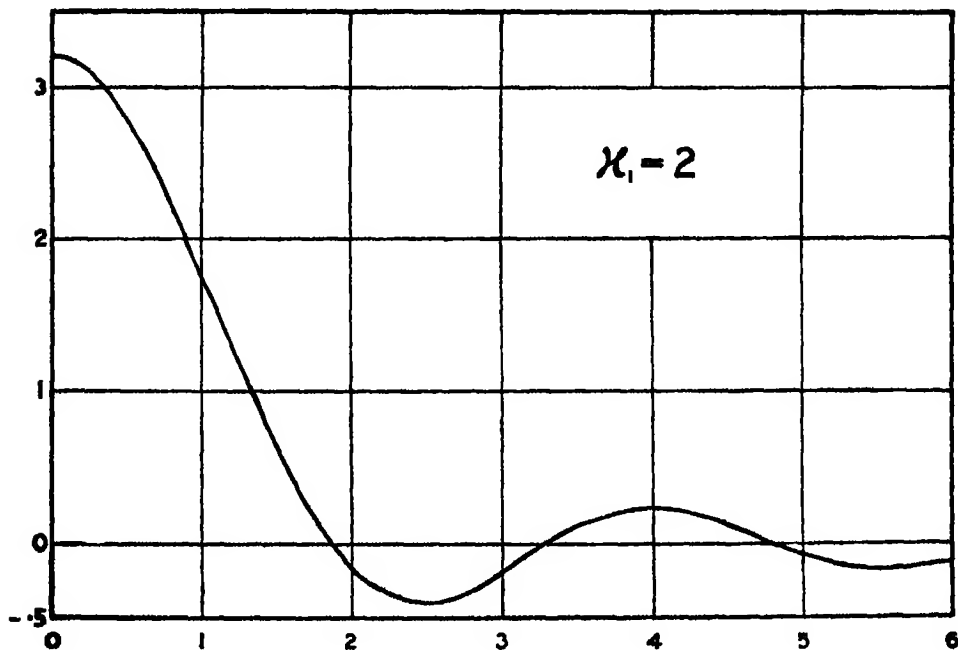
When $k_1 = 10$, $\phi(x) = \mathrm{Si}(10x+10) - \mathrm{Si}(10x-10)$.   (8)

We find

$$k_1 = 10.$$

x.	$\phi(x)$	x	$\phi(x)$	x.	$\phi(x)$
0·0	+3 3167	1·7	+0 1257	3 4	−0 0067
0 1	3 2433	1 8	+0 0305	3·5	+0 0272
0·2	3 0792	1 9	−0 0677	3 6	+0 0349
0·3	2 9540	2 0	−0 0916	3 7	+0 0115
0 4	2 9809	2 1	−0 0365	3 8	−0 0203
0·5	3 1681	2 2	+0 0393	3 9	−0 0322
0·6	3 3895	2 3	+0 0709	4 0	−0 0151
0·7	3 4388	2·4	+0 0390	4·1	+0 0142
0·8	3 1430	2 5	−0 0213	4·2	+0 0393
0·9	2 4647	2 6	−0 0562	4·3	+0 0178
1 0	1 5482	2 7	−0 0415	4 4	−0 0069
1·1	0 6466	2 8	+0 0069	4·5	−0 0362
1·2	+0 0107	2 9	+0 0447	4 6	−0 0194
1·3	−0 2532	3 0	+0 0387	4·7	+0 0068
1 4	−0 2035	3 1	+0 0000	4 8	+0 0230
1·5	−0 0184	3 2	−0 0358	4·9	+0 0206
1·6	+0 1202	3 3	−0 0371	5 0	−0 0002
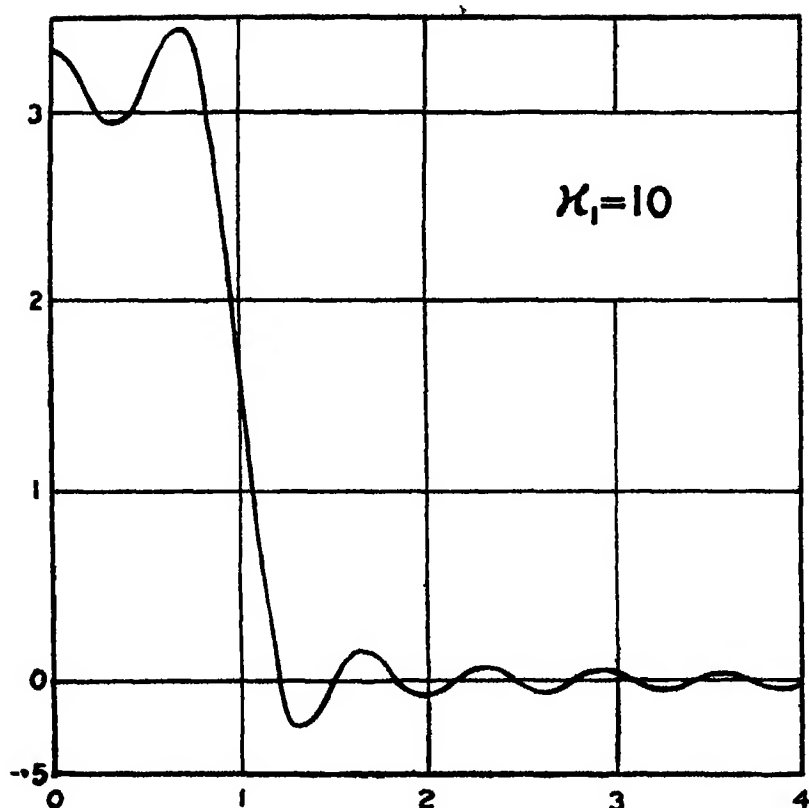
The same set of values of Si up to $S_1(60)$ would serve also for the calculation of $\phi(x)$ for $k_1 = 20$ and from $x = 0$ to $x = 2$ at intervals of 0.05. It is hardly necessary to set this out in detail

An inspection of the curves plotted from the above tables shows the approximation towards discontinuity as k_1 increases.

That the curve remains undulatory is a consequence of the sudden stoppage of the integration at $k = k_1$ If we are content with a partial suppression only of the shorter wave-lengths, a much simpler solution is open to us. We have only to introduce into (1) the factor e^{-ak}, where a is positive, and to continue the integration up to $x = \infty$. In place of (2), we have

$$\phi(x) = \int_0^\infty \frac{dk\, e^{-ak}}{k} \left\{ \sin k\,(x+1) - \sin k\,(x-1) \right\} = \tan^{-1}\left(\frac{x+1}{a}\right) - \tan^{-1}\left(\frac{x-1}{a}\right).$$
(9)

The discontinuous expression corresponds, of course, to $a = 0$. If a is merely small, the discontinuity is eased off. The following are values of $\phi(x)$, calculated from (9) for $a = 1,\ 0.5,\ 0.05$:—

$$a = 1.$$

x	$\phi(x)$	x	$\phi(x)$	x	$\phi(x)$
0 0	1 571	2 ·0	0 464	4 0	0 124
0 5	1 446	2 5	0 309	5 0	0 080
1 0	1 107	3 0	0 219	6 ·0	0 055
1 5	0 727				

$$a = 0 \ 5$$

x	$\phi(x)$	x	$\phi(x)$	x	$\phi(x)$
0 ·00	2 214	1 ·00	1 326	2 ·00	0 298
0 25	2 173	1 25	0 888	2 50	0 180
0 50	2 111	1 50	0 588	3 ·00	0 120
0 75	1 756	1 75	0 408	3 50	0 ·087

$$a = 0 \ 05$$

x	$\phi(x)$	x	$\phi(x)$	x	$\phi(x)$
0 00	3 041	0 90	2 652	1 20	0 222
0 20	3 037	0 95	2 331	1 40	0 103
0 40	3 023	1 ·00	1 546	1 ·60	0 ·064
0 60	2 986	1 ·05	0 ·761	1 80	0 045
0 80	2 869	1 10	0 440	2 ·00	0 ·033

As is evident from the form of (9), $\phi(x)$ falls continuously as x increases, whatever may be the value of a

On the Theory of Long Waves and Bores.

By Lord Rayleigh, O.M., F R.S

In the theory of long waves in two dimensions, which we may suppose to be reduced to a " steady " motion, it is assumed that the length is so great in proportion to the depth of the water that the velocity in a vertical direction can be neglected, and that the horizontal velocity is uniform across each section of the canal. This, it should be observed, is perfectly distinct from any supposition as to the height of the wave. If l be the undisturbed depth, and h the elevation of the water at any point of the wave, u_0, u the velocities corresponding to l, $l+h$ respectively, we have, as the equation of continuity,

$$u = \frac{lu_0}{l+h}. \tag{1}$$

By the principles of hydrodynamics, the increase of pressure due to retardation will be

$$\tfrac{1}{2}\rho\,(u_0^2 - u^2) = \frac{\rho u_0^2}{2} \cdot \frac{2lh + h^2}{(l+h)^2} \tag{2}$$

On the other hand, the loss of pressure (at the surface) due to height will be $g\rho h$, and therefore the total gain of pressure over the undisturbed parts is

$$\left(\frac{\rho u_0^2}{l} \cdot \frac{1 + h/2l}{(1 + h/l)^2} - g\rho \right) h. \tag{3}$$

If, now, the ratio h/l be very small, the coefficient of h becomes

$$\rho\,(u_0^2/l - g), \tag{4}$$

and we conclude that the condition of a free surface is satisfied, provided $u_0^2 = gl$. This determines the rate of flow u_0, in order that a stationary wave may be possible, and gives, of course, at the same time the velocity of a wave in still water.

Unless h^2 can be neglected, it is impossible to satisfy the condition of a free surface for a stationary long wave—which is the same as saying that it is impossible for a long wave of finite height to be propagated in still water without change of type.

Although a constant gravity is not adequate to compensate the changes of pressure due to acceleration and retardation in a long wave of finite height, it is evident that complete compensation is attainable if gravity be made a suitable function of height; and it is worth while to enquire what the law of force must be in order that long waves of unlimited height may

travel with type unchanged. If f be the force at height h, the condition of constant surface pressure is

$$\tfrac{1}{2}\rho u_0^2 \left\{ 1 - \frac{l^3}{(l+h)^3} \right\} = \rho \int_0^h f\,dh, \quad \text{*} \tag{5}$$

whence

$$f = -\frac{u_0^2}{2} \cdot \frac{d}{dh}\frac{l^3}{(l+h)^3} = u_0^2 \frac{l^3}{(l+h)^3}, \tag{6}$$

which shows that the force must vary inversely as the cube of the distance from the bottom of the canal   Under this law the waves may be of any height, and they will be propagated unchanged with the velocity $\sqrt{(f_1 l)}$, where f_1 is the force at the undisturbed level *

It may be remarked that we are concerned only with the values of f at water-levels which actually occur.   A change in f below the lowest water-level would have no effect upon the motion, and thus no difficulty arises from the law of inverse cube making the force infinite at the bottom of the canal

When a wave is limited in length, we may speak of its velocity relatively to the undisturbed water lying beyond it on the two sides, and it is implied that the uniform levels on the two sides are the same.   But the theory of long waves is not thus limited, and we may apply it to the case where the uniform levels on the two sides of the variable region are different, as, for example, to *bores*   This is a problem which I considered briefly on a former occasion,† when it appeared that the condition of conservation of energy could not be satisfied with a constant gravity   But in the calculation of the loss of energy a term was omitted, rendering the result erroneous, although the general conclusions are not affected   The error became apparent in applying the method to the case above considered of a gravity varying as the inverse cube of the depth.   But, before proceeding to the calculation of energy, it may be well to give the generalised form of the relation between velocity and height which must be satisfied in a *progressive* wave,‡ whether or not the type be permanent

In a small positive progressive wave, the relation between the particle-velocity u at any point (now reckoned relatively to the parts outside the wave) and the elevation h is

$$u = \sqrt{(f/l)}\ h. \tag{7}$$

If this relation be violated anywhere, a wave will emerge, travelling in the

* 'Phil. Mag.,' vol. 1, p. 257 (1876) , 'Scientific Papers,' vol. 1, p 254.

† 'Roy. Soc. Proc.,' A, vol. 81, p. 448 (1908) , 'Scientific Papers,' vol 5, p. 495

‡ Compare 'Scientific Papers,' vol. 1, p. 253 (1899)

negative direction   In applying (7) to a wave of finite height, the appropriate form of (7) is

$$du = \sqrt{\left(\frac{f}{l+h}\right)} dh, \tag{8}$$

where f is a known function of $l+h$, or on integration

$$u = \int_0^h \sqrt{\left(\frac{f}{l+h}\right)} dh \tag{9}$$

To this particle-velocity is to be added the wave-velocity

$$\sqrt{\{(l+h)f\}}, \tag{10}$$

making altogether for the velocity of, e.g , the crest of a wave relative to still water

$$\int_0^h \sqrt{\left(\frac{f}{l+h}\right)} dh + \sqrt{\{(l+h)f\}} \tag{11}$$

Thus if f be constant, say g, (9) gives de Morgan's formula

$$u = 2\sqrt{g} \{(l+h)^{\frac{1}{2}} - l^{\frac{1}{2}}\}, \tag{12}$$

and from (11)

$$3\sqrt{g}\sqrt{(l+h)} - 2\sqrt{(gl)} \tag{13}$$

If, again,

$$f = \frac{f_1 l^3}{(l+h)^3}, \tag{14}$$

(11) gives as the velocity of a crest

$$\frac{f_1^{\frac{1}{2}} l^{\frac{3}{2}} h}{l+h} + \frac{f_1^{\frac{1}{2}} l^{\frac{3}{2}}}{l+h} = \sqrt{(f_1 l)}, \tag{15}$$

which is independent of h, thus confirming what was found before for this law of force.

As regards the question of a bore, we consider it as the transition from a uniform velocity u and depth l to a uniform velocity u' and depth l', l' being greater than l The first relation between these four quantities is that given by continuity, viz.,

$$lu = l'u' \tag{16}$$

The second relation arises from a consideration of momentum   It may be convenient to take first the usual case of a constant gravity g The mean pressures at the two sections are $\frac{1}{2}gl$, $\frac{1}{2}gl'$, and thus the equation of momentum is

$$lu(u - u') = \frac{1}{2}g(l'^2 - l^2). \tag{17}$$

By these equations u and u' are determined in terms of l, l' :—

$$u^2 = \frac{1}{2}g(l+l') \cdot l'/l, \qquad u'^2 = \frac{1}{2}g(l+l') \, l/l' \tag{18}$$

We have now to consider the question of energy   The difference of work

done by the pressures at the two ends (reckoned per unit of time and per unit of breadth) is $lu(\frac{1}{2}gl - \frac{1}{2}gl')$ And the difference between the *kinetic* energies entering and leaving the region is $lu(\frac{1}{2}u^2 - \frac{1}{2}u'^2)$, the density being taken as unity   But this is not all   The *potential* energies of the liquid leaving and entering the region are different   The centre of gravity rises through a height $\frac{1}{2}(l'-l)$, and the gain of potential energy is therefore $lu \; \frac{1}{2}g(l'-l)$ The whole *loss* of energy is accordingly

$$lu\left\{\tfrac{1}{2}gl - \tfrac{1}{2}gl' + \tfrac{1}{2}u^2 - \tfrac{1}{2}u'^2 - \tfrac{1}{2}g(l'-l)\right\} = lu\left\{gl - gl' + \tfrac{1}{4}g(l+l')\left(\frac{l'}{l} + \frac{l}{l'}\right)\right\}$$

$$= lu \; \frac{g(l'-l)^3}{4ll'} \tag{19}$$

This is much smaller than the value formerly given, but it remains of the same sign.   "That there should be a loss of energy constitutes no difficulty, at least in the presence of viscosity, but the impossibility of a gain of energy shows that the motions here contemplated cannot be reversed"

We now suppose that the constant gravity is replaced by a force f, which is a function of y, the distance from the bottom   The pressures p, p' at the two sections are also functions of y, such that

$$p = \int_y^l f \, dy, \qquad p' = \int_y^{l'} f \, dy \tag{20}$$

The equation of momentum replacing (17) is now

$$lu(u - u') = \int_0^{l'} p' \, dy - \int_0^l p \, dy = \left[p'y\right]_0^{l'} - \left[py\right]_0^l - \int_0^{l'} y \frac{dp'}{dy} \, dy + \int_0^l y \frac{dp}{dy} \, dy$$

$$= \int_0^{l'} yf \, dy - \int_0^l yf \, dy = \int_l^{l'} yf \, dy, \tag{21}$$

the integrated terms vanishing at the limits   This includes, of course, all special cases, such as $f =$ constant, or $f \propto y^{-3}$

As regards the reckoning of energy, the first two terms on the left of (19) are replaced by

$$lu\left\{\frac{1}{l}\int_0^l p \, dy - \frac{1}{l'}\int_0^{l'} p' \, dy\right\}. \tag{22}$$

The third and fourth terms representing kinetic energy remain as before For the potential energy we have to consider that a length u and depth l is converted into a length u' and depth l'.   If we reckon from the bottom, the potential energy is in the first case

$$u\int_0^l dy \int_0^y f \, dy,$$

in which $\qquad \displaystyle\int_0^y f \, dy = \int_0^l f \, dy - \int_y^l f \, dy = p_0 - p,$

p_0 denoting the pressure at the bottom; so that the potential energy is

$$ul\left\{p_0 - \frac{1}{l}\int_0^l p\,dy\right\}.$$

The difference of potential energies, corresponding to the fifth and sixth terms of (19), is thus

$$lu\left\{p_0 - p_0' - \frac{1}{l}\int_0^l p\,dy + \frac{1}{l'}\int_0^{l'} p'\,dy\right\}. \tag{23}$$

The integrals in (23) compensate those of (22), and we have finally as the loss of energy

$$lu\left\{p_0 - p_0' + \tfrac{1}{2}u^2 - \tfrac{1}{2}u'^2\right\} = lu\left\{\tfrac{1}{2}u^2 - \tfrac{1}{2}u'^2 - \int_l^{l'} f\,dy\right\} \tag{24}$$

It should be remarked that it is only for values of y between l and l' that f is effectively involved

In the special case where $f = \mu y^{-3}$, equations (16), (21) give

$$u^2 l^2 = \mu, \qquad u'^2 l'^2 = \mu, \tag{25}$$

the introduction of which into (24) shows that, in this case, the loss of energy vanishes, all the conditions can be satisfied, even though there be no dissipation   The reversed motion is then equally admissible

Experimental.

The formation of bores is illustrated by a very ordinary observation, probably not often thought of in this connection. Something of the kind may usually be seen whenever a stream of water from a tap strikes a horizontal surface   The experiment is best made by directing a vertically falling stream into a flat and shallow dish from which the water over-flows.* The effective depth may be varied by holding a glass plate in a horizontal position under the water surface. Where the jet strikes, it expands into a thin sheet which diverges for a certain distance, and this distance diminishes as the natural depth of the water over the plate is made greater. The circular boundary where the transition from a small to a greater depth takes place constitutes a bore on a small scale. The flow may be made two-dimensional by limiting it with two battens held in contact with the glass. I have not attempted measures. On the smallest scale surface-tension doubtless plays a considerable part, but this may be minimised by increasing the stream, and correspondingly the depth of the water over the plate, so far as may be convenient.

* The tap that I employed gives a jet whose diameter is 6 mm. A much larger tap may need to be fitted with a special nozzle.—May 14.

The Flow in Metals under Large Constant Stresses.

By E. N DA C. ANDRADE, B.Sc., Ph D., late 1851 Exhibition Scholar of
University College, London.

§ 1. The object of this research was to examine the general laws of flow in
metallic wires when extended in the region of large permanent set by stresses
kept constant throughout the flow   Previously[*] I have investigated in
detail the flow for one metal, lead, and put forward some empirical laws,
it was desired to see if these laws could be extended to other metals,
and especially to investigate the effect of temperature on the nature of the
flow.   For lead, rise of temperature causes a very rapid increase in the rate
of the viscous[†] part of the flow (*loc cit*), hence it seemed likely that at
very low temperatures the viscous part of the flow would cease altogether,
although large permanent extensions might be obtainable, and thus lead
might behave in this respect as iron behaves at atmospheric temperatures.
Similarly iron at a high temperature might behave like lead at atmospheric
temperatures.   It was also desired to see if very pure metals behaved in the
same way as commercial metals, for it has been supposed that the non-
viscous character of the initial part of the extension-time curve is due to
impurities   Further, the properties of the viscous flow itself were to be
investigated in greater detail

Investigations on these points are described in this paper, a summary of
the results will be found in § 10   Incidentally, in the case of alloys, a type
of flow not hitherto observed has been found.

§ 2. To test the flow under constant stress the device of the hyperbolic
weight was again employed.   By the use of such a weight, sinking as the
wire stretches into a liquid of suitable density, the effective load is diminished
in such a way that the stress over the cross-section remains constant as the
wire thins (see *loc. cit*).   For experiments at lower temperature the wires
were pulled upwards.   A vertical open glass tube, the upper end of which is
attached to a table, carries a bar at its lower end, to which the lower hook
of the wire-holders is fastened, the upper end is pulled upwards by fine
steel wires which pass over pulleys and carry the hyperbolic weight.   Round

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[*] E. N. da C. Andrade, 'Roy. Soc. Proc.,' A, vol. 84, p. 1 (1910).

[†] By viscous flow I refer throughout to that part of the flow for which the rate of
extension, per unit length flowing, remains constant, or $\frac{1}{l}\frac{dl}{dt}$ = constant, as would be
the case for a very viscous liquid.

this tube can be put any heating or cooling bath   For use with a sulphur bath the glass tube was replaced by a closed iron tube   The liquid employed for the hyperbolic weight, in the case of large loads, was mercury   For the higher temperatures an electric furnace was used, and the wire arranged horizontally   It was enclosed in a tube of combustion glass which projected some distance from the furnace at each end, the joints, where the wire-holders passed out of the tube, were made close with thin rubber, so that in cases where the specimen was to be kept clean for microscopic observation a stream of hydrogen could be maintained through the tube during the experiment   The temperature was measured with a thermocouple.

§ 3. The metals investigated were —Lead, as being a metal which shows well at room temperature all the features of the flow in metals, viz, the immediate stretch, the β-flow, and the viscous flow, tin, as the second component in the alloy investigated; iron and copper, as showing very little viscous flow at room temperature, mercury, because it can be easily obtained very pure, and a lead-tin alloy and a brass to represent alloys, which were found to behave anomalously, a few experiments were also done on German silver, as a three-metal alloy

All the metals, except mercury, were bought in the form of wires   For mercury two hollow glass hooks were connected to a thin glass tube with rubber, and the whole poured full of mercury and then immersed in a bath of solid carbon dioxide and alcohol.   When the mercury was frozen solid the whole was removed from the bath, and the glass tube, previously scored with a diamond, quickly broken off, the mercury wire so obtained with a hook at each end was replaced in the bath, and subsequently stretched just like any other wire.

Series of observations were made at different temperatures with all the metals mentioned to obtain the law connecting extension with time, experiments at different stresses being performed at each given temperature Constancy of stress in any one experiment was secured by means of a suitable hyperbolic weight

The iron and copper wires were carefully annealed, and after this treatment gave consistent results   Lead anneals itself at room temperature, that is, lead wires which have been left unstrained for a considerable time always give consistent results.   Experiments on a piece of the lead wire used in 1909 gave results agreeing with those already published.

§ 4. It was found that without exception all the single metals—not alloys —gave at the various temperatures investigated curves of extension against time which could be closely represented by the formula

$$l = l_0 (1 + \beta t^{\frac{1}{3}}) e^{\kappa t},$$

given in the former paper, by assigning suitable values to the constants
Deviations of the calculated from the observed values in no case exceed, at
any point of the range, 2 per cent of the whole extension, and in most cases
such deviations are less than 1 per cent. of the total extension, which, con-
sidering possible small variations from constancy of stress, is well within
experimental error *   The final extensions obtained ranged up to about
20 per cent of the original length for most metals and temperatures, but
were occasionally larger, tin at room temperature being extended by 40 per
cent. for instance

The constants l_0, β, k are not purely artificial, but to each corresponds a
physical process, and it would be impossible to get a curve to represent all
the cases with less than three constants l_0 represents the immediate length
on loading.† β is the coefficient which gives a measure of that part of the
flow whose rate decreases as the time increases, and k measures the final
flow which proceeds viscously   The exponential form of the viscous term
follows from the condition $\dfrac{1}{l}\dfrac{dl}{dt} = \text{constant}$

At low temperatures k is zero for all metals investigated even with the
greatest stresses which could be applied without breaking the wire β is
very small at low temperatures for all stresses, probably zero if the
temperature is taken low enough l_0, however, can in general for larger
stresses be obtained as great as at higher temperatures (without breaking the
wire), thus lead wires loaded at $-180°$ C acquired considerable permanent
set—up to 15 per cent. of the original length—and copper wires loaded
at $-78°$ C were extended by similar amounts, but in such cases nearly
the whole set takes place as soon as the load is applied.   The very
small subsequent flow does not become viscous with increasing time,
but soon ceases to be perceptible.   The form of curve for very low
temperature is probably composed of a straight line of length l_0 along the
axis of l, representing the immediate extension, and a straight line parallel to
the time axis at a distance l_0 This is closely approached by lead at $-180°$ C.
and iron at $15°$ C. for all stresses.

As the temperature is taken higher the β-flow becomes more considerable,
but there is still no viscous flow (*cf.* lead at $-78°$ C., fig. 1).   At a higher
temperature we get the normal curve showing immediate extension, β-flow,

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* Deviations as large as 2 per cent. only occur in the earlier part of the curve,
i.e. the first two minutes or so, where experimental errors are necessarily larger, owing
to small unavoidable differences in the way in which the load is applied.

† Throughout the wires will be considered as of unit length before application of
stress, thus $l_0 - 1$ represents the immediate extension.

and final flow of the viscous type. Considering the curves for different stresses at such a constant temperature, for increasing stress the constant β first increases slowly, then rapidly, and finally tends to a constant limiting value k increases slowly at first, and then much more rapidly, as shown in the diagram representing the values of the constants for different stresses at constant temperature for lead (fig 4). At a higher constant temperature the viscous flow becomes the preponderating factor; β again for increasing stress increases to a constant limit, which has the same value as for the lower temperature. k increases without limit   Thus with increasing temperature and stress β reaches a limit, while k increases finally very rapidly with both temperature and stress. The time-extension curves for lead, which are typical for all the single metals investigated, are given for the various temperatures in figs 1, 2, and 3,* the variations of the constants of the formula with stress for the different temperatures are given in fig 4 The constants for copper at 410° C show the same features, β approaching a constant value, k increasing without limit

The extension-time curves for mercury at $-78°$ C are intermediate in type between those for lead at 160° C and 17° C   The variation with stress could not be obtained, as, owing to the difficulty of annealing the mercury wire, we did not always get the same extensions on repeating with a fresh wire at the same stress , the type of curve, however, remained the same, and could always be represented by the formula. The mercury, being carefully distilled metal, is very pure, and these experiments show that the non-viscous form of the initial part of the curve is not in any way due to impurities in the metals

The curves for iron at 444° C resemble those for lead at 16° C , there is no difference of type   Thus the behaviour of iron is not anomalous, as suggested by P. Phillips† from observations on small extensions at room temperature , it merely shows the low temperature type of flow, represented by lead at $-180°$ C, at ordinary temperature.

The main result of this part of the work is to show that typical metals of widely different nature obey the same general laws of flow, the apparent difference of type disappearing when a wide range of temperature is considered. The higher the temperature for a given metal the more the viscous type of flow predominates.   Small impurities do not affect the general type of the extension curves , pure mercury at $-78°$ C has much the same curves as soft commercial iron at 444° C.

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* Only the initial portions of the curves are shown, the time of observation in many cases extended over hours.

† 'Phil. Mag,' April, 1905, p. 513.
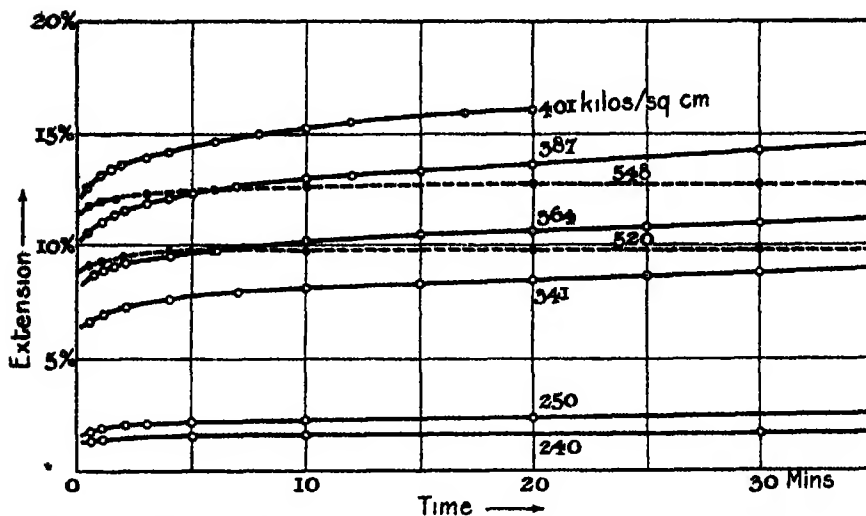
Fɪɢ 1—Lead at −180° and at −78° C   (The dotted curves refer to −180°, the continuous curves to −78° C)
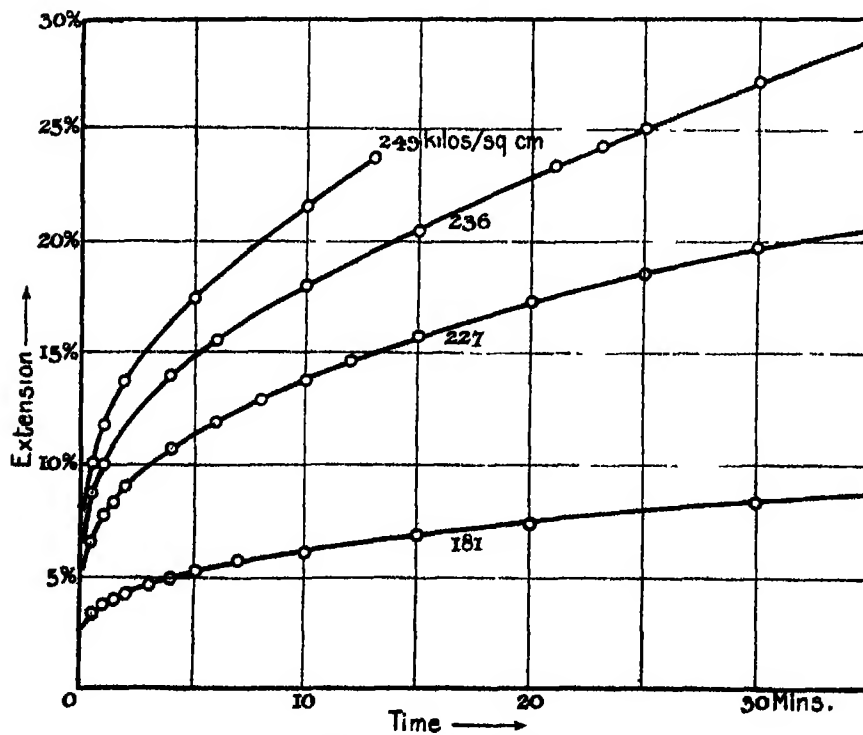
Fɪɢ 2—Lead at 17° C
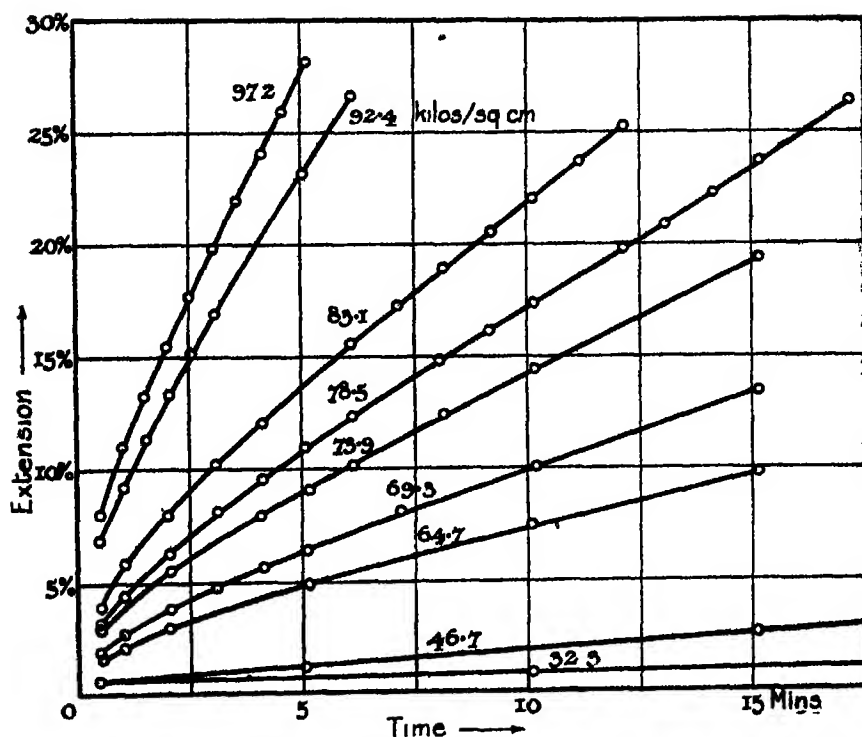
Fig 3 —Lead at 160° C
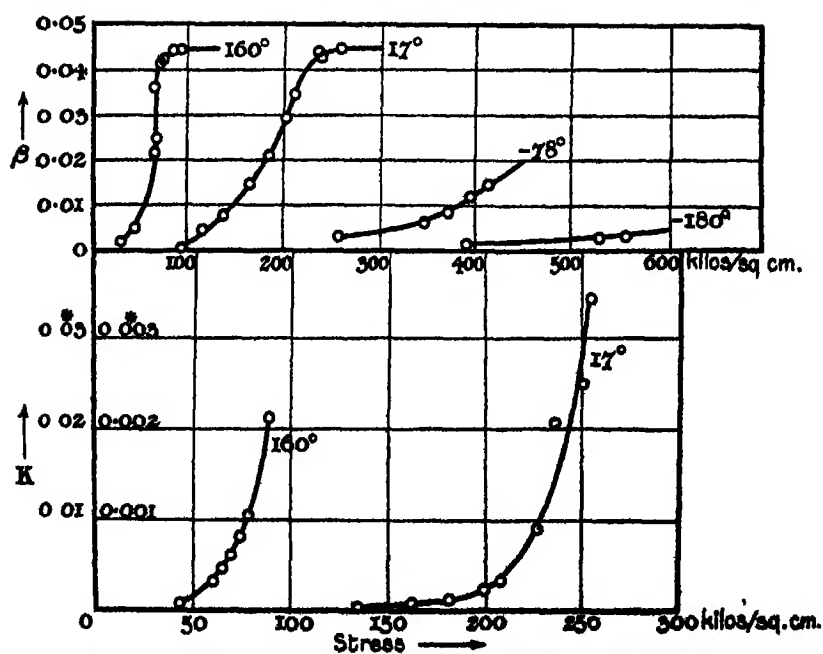
Fig 4.—The Constants β and K for Lead at different Temperatures.

* *Note.*—The ordinates for the K curve at 160° are given on the left, at 17° on the right, of the axis of K.

The values of the constants for the different metals at the various temperatures and stresses are given in Table I on p 336

§ 5 When a lead-tin alloy (fuse wire, 21 5 per cent lead, 78 5 per cent. tin) was investigated at room temperature it seemed to give curves which could be fitted by the law $l = l_0 (1 + \beta t^{\frac{1}{2}}) e^{kt}$, the immediate extension $l_0 - 1$, and β being very small indeed, that is, the flow was of the viscous type almost from the start * At -180° C the alloy gave a curve resembling that for lead at this temperature, the extension nearly all taking place in the first moment, the extension could not, however, be obtained as great as for, lead, the wire breaking first   But at an intermediate temperature, -78° C, the extension-time curves presented features not hitherto observed, there was very little immediate extension, the stretch started slowly, then became more rapid, and finally decreased again, the rate approaching a constant value, *i e*, the flow finally becoming viscous   The form of the curve is shown in the series of curves for fuse wire at different stresses at a temperature of -78° C in fig 5   The experiments on wires of pure tin at -78° C showed that for
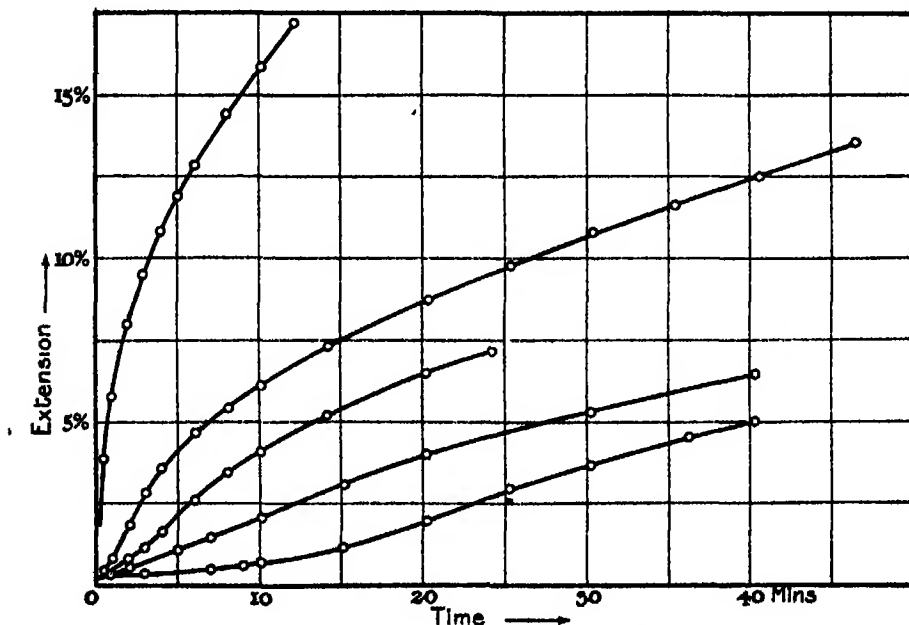
Fig. 5 —Lead-Tin Alloy at -78° C

this metal the flow is of the type represented by the formula if $l_0 - 1$ and k are small, thus neither component of the alloy presents peculiarities at this . temperature to account for the form of the curves   The alloy shows a

* See ' Roy. Soc. Proc.,' A, vol. 84, p 5 (1910).

TABLE I

Temperature	Stress.	l_0.*	β	k
Lead Area of cross section (at 20° C), 2 16 sq mm				
	kilos /sq cm			
−180° C	388	1 050	0 ·0012	0
	520	1 ·001	0 0022	0
	548	1 ·118	0 ·0025	0
−78° C	250	1 ·017	0 ·0026	0
	341	1 ·066	0 0060	0
	364	1 081	0 0085	0
	367	1 102	0 0115	0
	401	1 118	0 0142	0
17° C	181	1 ·014	0 021	0 ·000115
	227	1 ·037	0 040	0 000690
	236	1 052	0 046	0 ·00190
	249	1 070	0 045	0 00350
160° C	32 3		0 ·0020	0 00010
	46 7		0 0045	0 00095
	64 7		0 0210	0 0032
	69 3		0 024	0 0048
	73 9		0 041	0 0060
	78 5		0 041	0 0083
	83 2		0 043	0 0106
	92 4		0 ·043	0 ·0216
Copper Area of cross-section (at 20° C), 0 155 sq mm				
−78° C	2548	1 143	0 002	0
15° C	1696	1 ·037	0 0013	0
	1865	1 ·070	0 0014	0
	2287	1 1156	0 0021	0
410° C	217		0	0
	522		0 0035	0 00018
	783		0 0080	0 00090
	957		0 ·0090	0 00240
	1044		0 ·0089	0 ·00460
	1131		0 0085	0 00680
Tin Area of cross-section (at 20° C), 0 915 sq mm				
20° C	119	1 ·000	0 0066	0 0021
	191	1 ·000	0 0780	0 ·0042
−78° C	321	1 ·000	0 0140	0
	386	1 0027	0 0225	0 ·00032
Iron Area of cross-section (at 20° C.), 0 204 sq mm				
444° C	956	1 0015	0 0005	} 0 00000
	1195	1 0030	0 ·0012	
	1435	1 ·0080	0 ·0037	
	1650	1 ·0030	0 ·0070	
	1920	1 ·0115	0 ·0123	0 ·00003
	2160	1 0170	0 ·0170	0 ·00006
	2400	1 0180	0 ·0210	0 00033

* The values of l_0 have not been determined accurately, as this would need special precautions
They are given, however, as some indication of the amount of immediate extension

softening soon after application of stress, instead of the usual hardening, such a softening of a metal has not, as far as I am aware, been previously observed.

Curves of this form were sought with brass, as another two-metal alloy, and were obtained at temperatures of 350° C. and 400° C. At higher temperatures the flow was of the viscous type, almost from the start obeying the law $l = l_0 e^{kt}$, as with fuse wire at room temperature. For both these alloys the curves at low temperature were of the type of lead at $-180°$ C., only at low temperature under large stresses is there marked immediate stretch.

A few experiments were carried out with German silver as a three-metal alloy. At 565° C. and 455° C. the curves were of the purely viscous type, showing neither immediate extension nor β-flow, at 355° C. they were of the type of lead at $-78°$ C. No new features were discovered.

§ 6. It has been shown that for metals the flow tends to become in every case finally viscous (if it does not become zero, which may be considered as a special case with a zero coefficient λ). The question arises as to what change is produced in the metal which sets it in a condition to flow viscously, and how the change can be effected. Lead was used for a series of experiments. It was found that by extending the wire rapidly under a large stress for a short time it can be put in a condition to flow viscously from the start when subject to a smaller stress. The more rapid the preliminary extension, assumed to be of the same amount in all cases, the smaller the rate of the viscous flow under the subsequent smaller stress, this rate, however, reaches a lower limit, after which increased rapidity of preliminary extension produces no further hardening, as tested by the smaller stress.

It might be supposed that the variation of λ with stress at constant temperature does not express a physically simple relation because the wire, when the purely viscous flow sets in, is not in the same state for the smaller stresses as for the larger ones, it having been subjected to less preliminary strain in the former cases. Experiments were therefore carried out to ascertain the relation between the viscous rate and the stress when the wires were all subjected to the same treatment to bring them into a state such that, on being loaded, the flow was of the viscous type. A series of wires were all extended the same amount (about 18 per cent.) by the same stress, these wires were then subjected to various smaller stresses, under which they began to flow viscously almost from the start. The rate of viscous flow for the various stresses was plotted against the stress. The curve obtained was not very different from that of k against stress, in which case each stress is left to bring the wire to the viscous state of itself.

The curve is far from being linear. But it is not necessary to assume that

the law of flow in the individual crystals of the metal is other than linear with the stress when the crystals have once been brought to flow viscously. An explanation of the form of the curve based on the assumption that the stress required to cause viscous flow of any single crystal depends upon its size will be given in § 9

§ 7 It has also been found that severe preliminary twisting will put the wire in a state to give the flow viscous almost from the start With increasing amount of preliminary twist the rate of flow first of all decreases, but reaches a minimum and then increases slowly, probably owing to tears in the metal A twist of a given number of turns is more effective in hardening the metal if it is applied half in the one direction and then half in the other, than if it be applied all in the one direction These experiments were carried out on lead, the twists causing permanent set All this tends to show that any form of severe preliminary strain will condition the flow of the viscous type, and that with increasing severity of treatment the rate of this subsequent flow decreases to a constant final value

§ 8. A series of microphotographs were taken of specimens of lead prepared by squeezing scraped lead wires between hot plate glass The strips were extended by equal amounts, about 12 per cent, some at − 180° C, some at 16° C, and some at 160° C, to see if difference in the structure could be discovered. Others were taken of strips of soft armature iron extended at 16° C and at temperatures from 400° C. to 600° C, these were polished before the extension, which took place in an atmosphere of hydrogen The structure was in all cases sufficiently revealed by the straining without etching

The main object was to see if slip bands were formed equally at the different temperatures, and, in general, if the different types of flow were attended by different types of subsequent structure The photographs of iron showed slip bands formed with equal distinctness and frequency at both the higher and the lower temperatures. Although in the one case the extension, equal in all cases, occupied some minutes, and in the other was produced all at once, it was not possible to distinguish between the photographs. With lead the specimens extended at 160° C showed a somewhat coarser crystalline structure than those for lower temperatures In this case, as the flow was to last some minutes, only small stresses were applied, a finer structure would perhaps be produced if the largest stresses possible were used It was observed that at room temperature more rapid extension seemed to give a finer structure than one of equal magnitude less rapidly effected

Owing to differences between individual specimens, and parts of the same

The Flow in Metals under Large Constant Stresses. 839

specimen, small differences of structure may pass undetected, there is, however, no considerable difference to be observed in the formation of slip bands at the different temperatures   This accords with the theoretical considerations of the next paragraph   The formation of slip bands does not necessarily condition a viscous flow , it is merely a necessary preliminary, which may or may not be followed by such a flow, according to the temperature

§ 9 The work of Quincke,* Beilby,† Ewing and Rosenhain,‡ and Faust and Tammann§ has thrown much light on the structure and the process of plastic yield of metals, and their results are connected with many of the effects described in this paper   Even in the purest metals there are well-defined crystals separated from one another by thin walls (Quincke's " Schaumwande ") of non-crystalline material   These walls consist, in the case of pure metals, of an amorphous allotropic modification of the pure substance ; in other cases they contain in addition such small impurities as may be present   Beilby has shown that mechanical working of the surface or internal displacements, such as the relative slipping of the lamellæ of which a crystal is composed, produce fresh layers of the amorphous material, which is much harder than the crystalline form

We can on this explain the form of the extension-time curve, and the physical meaning of the constants l_0, β, h

When the wire is loaded there is an immediate stretching due to a large number of slips between the crystals and the lamellæ of crystals best disposed for slipping, with a consequent formation of layers of hard amorphous material   According to observations of Ewing and Rosenhain (_loc cit_) and Faust and Tammann (_loc cit_), which have been confirmed by the author for lead, the first slip bands appear normal to the direction of pull, and accordingly it appears that lamellæ which have this direction slip easiest   Owing to the formation of the hard layers between such lamellæ a redistribution of internal stress in the wire ensues, and other crystals not so favourably disposed for slip are now subject to forces large enough to cause slip and consequent hardening   Such a process continues as long as new crystals are being subjected to forces sufficient to cause the lamellar breakdown   This slipping, after the first immediate extension, constitutes the β-flow, and if the amorphous phase, when formed, can at the given

* For a summary of Quincke's work see G Quincke, "Die Schaumstruktur der Metalle," 'Internat Zeitsch. f Metallographie,' III, 1, p 23 (1912)

† 'Roy Soc. Proc,' A, vol 72, p. 218 and p 226 , vol 74, p 462 , vol 79, p 463 , vol 82, p 599

‡ 'Phil Trans ,' A, vol. 193, p. 353,

§ Zeitsch f Physik. Chemie,' vol 75, p 108 (1911)

temperature support the applied stress without yielding, with the slipping of the last lamellæ the flow comes to an end   The final number of layers formed increases with increase of applied external stress, as all the internal stresses are proportionally increased and consequently exceed the minimum value required to produce slip for crystals not included for smaller stresses It appears from the experiments described that there is a limit, however, to the amount of breaking up into lamellæ which can take place in a crystal after the immediate extension has occurred, the number of elementary crystals which can be subsequently produced by stress does not increase indefinitely   The number produced by a given constant stress increases to a limit with the time, and with increasing stress these limits increase to another limit, corresponding to the formation of all possible elementary crystals *   This is represented by the limit to which β tends with increasing stress   If the amorphous phase, although harder than the original crystals, can yet flow under the applied stresses it proceeds to do so wherever it has been formed linearly with the time, and gives the viscous or k flow   At low temperatures the amorphous material is too hard to flow   The different forms of curves are caused by the amorphous phase becoming softer relatively to the crystalline as the temperature rises †   There is obviously no limit to the rate of viscous flow   The theory will also account for the results on the effect of preliminary twisting and stretching (see §§ 6 and 7) in bringing the metal into a state to flow viscously   For such preliminary working results in the formation of the amorphous phase due to the breaking up of the crystals, so that the β-flow process has been already carried out, with increased working we should expect to reach a limit of hardening, when all possible amorphous layers have been formed   This is what has been found

The non-linear character of the curve connecting viscous rate and stress, when the wire has in each case been initially brought to the same state (§ 6), can be explained by the differences of size which exist among the crystals in one piece of metal   While the forces due to the external load acting on different crystals must be assumed to be proportional to their cross-sections, the forces of frictional resistance are independent of these cross-sections   If each crystal requires the same minimum force to act on it before it can begin to flow viscously, and the rate is then proportional to

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* Crystals which cannot be further broken up by stress   If viscous flow cannot take place at the given temperature, further increase of strain leads to tears in the metal and subsequent rupture.

† The effect of increase of stress is similar to that of increase of temperature, in that it increases the importance of the viscous flow relative to the β flow ; see curves.

the excess force, then flow will take place among the larger crystals of the wire for smaller stresses (applied to the wire as a whole) than are necessary to cause flow in the smaller ones   Increasing the stress causes a proportionate increase in the rate of flow of crystals already flowing, and in addition sets up the flow in fresh crystals   When practically all the crystals are flowing we should expect a linear increase of rate of flow with stress, to which the experimental curve actually approaches

In the case of alloys, to a difference in type of structure, as revealed by microphotographs, corresponds the difference in type of flow which has been demonstrated   Duplex alloys, such as the lead-tin alloy employed, have a ribbed structure, bands of light component (tin) and dark component (eutectic) running in and out of one another and interlocking *   The structure is thus somewhat analogous to a ferro-concrete block containing a large number of connected iron bars   On the application of large stresses the ribs of the harder component (eutectic), corresponding to the iron, must be broken before any flow can take place, this breaking is followed by a more rapid flow which corresponds to the softening of the metal which takes place in the initial stages of the flow at suitable temperatures (lead-tin, 78° C , brass, 400° C)   There is no evidence to be seen in Ewing and Rosenhain's photographs for the formation of large slip bands such as those in the single metals   Hence at high temperatures, when both components are soft, the flow takes place viscously from the start, there being very slight, if any, formation of the coarse bands which give rise to immediate yield and β-flow for the single metals

It is not claimed for the formula $l = l_0 (1 + \beta t^{\frac{1}{3}}) e^{kt}$ that it is more than an empirical formula representing the flow in single metals very closely in all cases $t^{\frac{1}{3}}$ should probably be replaced by a function of t which approximates closely to $t^{\frac{1}{3}}$ until t becomes very large, but approaches a constant limit as t approaches ∞ Until we know more concerning the mechanism of the slip we cannot profitably attempt to calculate a theoretical form for the curve , it may, however, be suggested that the method of approaching the problem will have to differ from those previously attempted in being a statistical one, taking account of the different sizes and dispositions of the crystals.

We have thus brought evidence to show that the laws of flow in single metals and alloys are intimately connected with their structure ; in all cases there are two components of quite different physical properties to be considered, and their variation in relative quantity and relative softness with the temperature accounts for the various experimental results obtained. Metals are not homogeneous, but they are essentially distinguished in respect

* *Cf* Ewing and Rosenhain, *loc. cit* , figs 47 and 48

of their flow from homogeneous substances not by their ability or inability to flow, which is simply a question of temperature, but by the laws which govern this flow as regards both time and stress.

§10. *Summary of Results*

(1) If wires of single metals be extended by large stresses, precautions being taken to keep the stress constant as the wire thins, the length at any time t can be expressed by the empirical formula

$$l = l_0 (1 + \beta t^{\frac{1}{3}}) e^{kt}$$

(2) Wires of pure distilled mercury in the solid state obey the same law, showing that this behaviour is not due to impurities in the metals.

(3) The various forms of extension-time curves which are observed for different metals at room temperature can all be obtained with one metal (lead) by suitably choosing the temperature, the constants of the formula varying with the temperature

(4) At a given temperature with increasing stress the constant β tends to a constant value , the constant k increases at a rate which itself increases to a constant value

(5) From experiments on lead it appears that the limit to which β tends with stress does not increase with the temperature   The limit cannot, however, be attained at low temperatures, owing to the wire breaking first

(6) Large preliminary strain, whether of extension or rotation, puts the wire in a state to flow viscously

(7) Duplex alloys, which possess a microstructure quite different from that of single metals, give a correspondingly different form of extension-time curve , the wire softens at a certain stage of the flow, instead of continually hardening up to a limit, as do the single metals

(8) On the basis of the co-existence of two different phases, the crystalline and the amorphous, the results have received a qualitative explanation

On the Properties of Magnetically Shielded Iron as Affected by Temperature.

By Ernest Wilson

In a paper recently read before the Society,[*] it was shown that if a specimen of stalloy in ring form is placed within an iron shield and then subjected to a magnetic force of about 2 CGS. units, its permeability is increased Moreover, careful demagnetisation was found to increase the permeability at the low forces at the expense of permeability at the higher forces Further experiments have been made with the same material in ring form at high temperatures It was thought that if the stalloy, when its temperature passes through the value at which the magnetic quality is regained on cooling, was simultaneously subjected to a magnetising force and shielded from the influence of the earth's magnetism, the permeability might be increased further This has been found to be the case

[*Note added May* 7, 1914.—My attention has been called to a paper by Messrs H Pender and R L Jones on "The Annealing of Steel in an Alternating Magnetic Field" These authors have obtained high values of the permeability (see the 'Physical Review,' 2nd Series, April, 1913, vol 1, No 4)]

In an earlier paper[†] experiments were described in connection with two small stalloy rings which have been used in the present experiments

In Table I the present experiments are numbered in the order in which they were made, and the curves are numbered in correspondence with them

Ring No 1

The specimen, which had been heated several times above the temperature at which magnetic quality is lost, was wound with an asbestos-covered wire and placed in a small iron box, the whole being heated in a gas furnace to the neighbourhood of 800° C About two hours were required to heat the specimen It was allowed to cool inside the magnetic shield previously used and described (*loc cit*), and at the same time it was subjected to a steady magnetising force of 3 12 CGS units. About five hours were required to cool it to atmospheric temperature. When at atmospheric temperature the specimen was taken out and tested for magnetic permeability The figures were obtained whilst gradually reducing the force and are given in Table I,

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[*] 'Roy. Soc Proc.,' A, vol 90, p. 179 (1914)

[†] 'Phys. Soc. Proc,' vol 23, Part 4, p 253, June 15, 1911

Table I—Permeability

Ring No 1

Expt Hmax	1. Just after being taken out of furnace B	1. μ	2. After being re-wound B	2. μ	3. After demagnetisation from H = 4 17 B	3. μ	4. After being polarised at H = 6 16 and subjected to vibrations B	4. μ
0·0105			2·67	254	4 81	457	3 29	312
0·0209			6 15	294	11 8	563	7 89	378
0·0522			23	441	42 8	820	34 2	655
0 105			63 8	606	116	1105	103	982
0 223	314	1060	209	935	369	1655	365	1640
0·311	2072	5630	397	1275	727	2345	748	2400
0·366					1150	3150	1210	3310
0 418	4030	8900			1870	4470	1920	4600
0 471					2710	5760	2750	5830
0 570	5910	10140	3892	7660	4280	7510	4360	7640
0·617			5140	8350	4840	7840	4920	7980
0·726	7590	9370	6860	8560	5905	8140	6040	8320
0·930			7590	7890	6665	8020	6780	8170
0·963			8160	7080	7540	7640		
1 16	8970	7190	8780	6500	8100	6980	8200	7070
1 99	10900	4720			8700	6280	9300	5920
2 41	10500	3490	10030	4300	9960	4180	9860	4670
3 81			10560	2930	10660	2800	10460	3780
6 16			11100	1950	11200	1890	11050	2480
12							11940	995
31 4							12900	408
45 6							13200	290

Ring No 3

Expt Hmax	11. After polarisation to H = 174 in shield B	11. μ	12. Demagnetised from H = 2 and resting all night B	12. μ
0·00343	0 994	292	1 45	422
0·00687	2 01	293	2 98	435
0 0115	3 53	307	5 33	464
0 0228	7 96	349	12 1	531
0·0571	25 4	444	48 1	843
0 115	65 9	573	139 6	1214
0 243	218	898	482	1394
0 394	459	1170	964	2450
0 674	4280	6350	3250	5690
0·800	5430	6790	5440	6800
0·915	6320	6900	6320	6900
1·03	7060	6860	7010	6800
1 25	7920	6710	7600	6700
1 16	8700	6350	8370	6410
1 34			9990	5660
1·76			12250	3980
3 12			13650	2930
4 66			14300	2580
5 54			15500	1580
9 79			15850	1520
10 45			16800	965
17 42			17970	466
38 54			18540	388
50 4			19300	248
77·7			20340	170
119 5				

Table I—*continued*

Ring No 2

Expt. Hmax	5. Before heat treatment		6. After annealing in shield without magnetising force		7. After demagnetisation from H = 3·2 at 50 frequency		8. Just after being taken out of furnace		9. After re-winding but otherwise not treated		10. After demagnetisation from H = 8·05	
	B	μ	B	μ	B	μ	B	μ	B	μ	B	μ
0·00688	3·95	376	3·2	906	2·96	262			1·72	252	2·87	420
0·0139	9·8	471	6·91	332	6·66	321			3·39	283	5·75	414
0·0275	35·5	683	25·8	496	27·4	527			8·62	313	15·5	564
0·0689	93·3	905	71·1	690	82	796	11·4	194	34·5	501	58	842
0·129									88·6	688	151	1173
0·138							45·8	281	98·6	715	160	1160
0·2095	277	1250	218	1000	261	1200	158	501	366	1250	606	2060
0·345			364	1170	503	1610	*788	2400	817	2370	853	2470
0·414							2150	4910	1330	3210	1475	3560
0·483									2450	5070	2350	4870
0·552							4520	8510	3350	6060	3390	6140
0·621	2610	4250	1220	1990			6020	9540	4090	6580	4150	6610
0·759			3180	4400	2890	3890	7390	10480	5490	7230	5470	7210
0·814			4010	4800	3300	4570	8090	10200	5920	7270	5870	7210
0·906					4080	4880			6780	7020	6720	6960
1·10	5830	5020	5140	4940	5150	4850	9340	8810	7370	6700	7340	6670
1·31	6070	5100	5670	4850	5650	4830	9650	8400	8030	6130	8110	6190
1·54			5950	4800			10300	7620	8610	5590	8680	5640
2·04			8160	3780	8160	3670	10440	6910	9790	4800	9430	5300
2·65	8760	3420	8720	3820			10890	5750	10360	3910	9660	4800
3·38	9650	2480					11040	4990	10650	3210	10380	3900
4·81					9900	2520	11800	3420			10700	3170
5·86	10900	1860									11200	2900

* Obtained after the force had been put back from 0·488 to 0·315

Experiment 1, and plotted in Curve 1   In all the other experiments the force
has been increased gradually.   It will be seen that the permeability rises
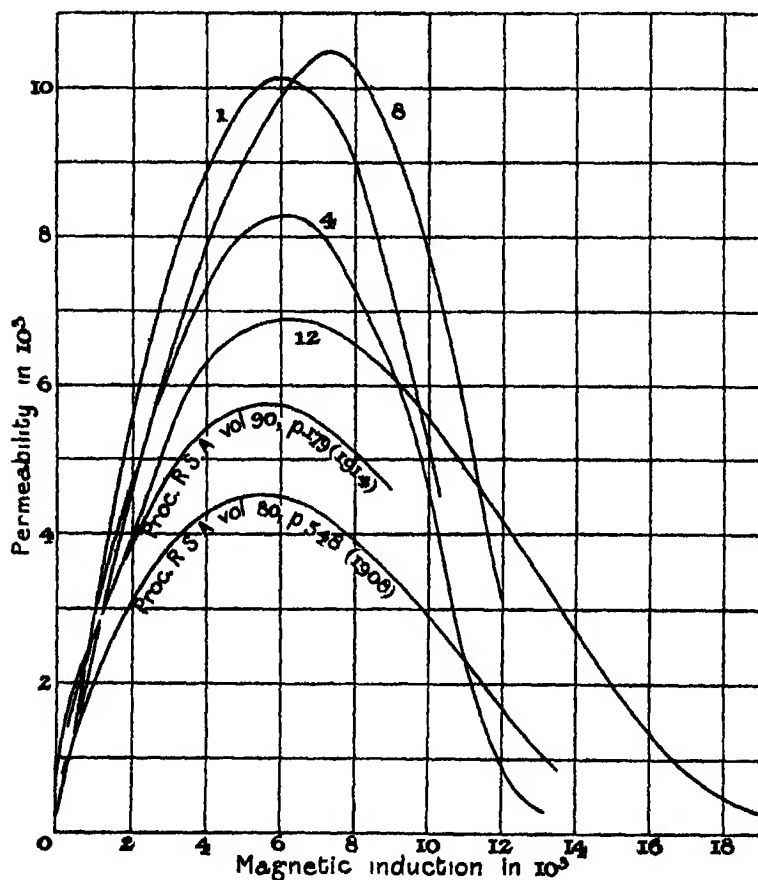
to about 10,000   The ring was then stripped and re-wound with cotton-
covered primary and secondary windings, the secondary winding being next
to the stampings, and this operation gave rise to considerable mechanical
disturbance   Experiment 2 shows that the maximum permeability has
dropped to 8330, and the initial permeability is small   On demagnetising
the specimen (Experiment 3) the effect previously observed is produced,
namely, the initial permeability is increased and the maximum reduced
On again polarising the specimen with a force of 6·16 and leaving it for
four days the ring was subjected for about half an hour to a high alternating
force having a maximum of 24 C G S. units at 80 complete periods per
second.   This caused the plates to vibrate and give the characteristic
sound   After an interval of two days Experiment 4 was then made.   It

will be seen that the maximum permeability went up to 8320, and that the initial value was lower than in Experiment 3 Experiment 4 also includes the taking of a few hysteresis loops, the particulars of which are given in Table II In the same table are also given figures taken from a normal specimen of stalloy which had been demagnetised most carefully * The maximum values of the magnetic induction happen to be very nearly the same It will be noticed that the coercive force H_0 in the present experiments is smaller for this value of the induction, whereas the residual magnetism B_0 is larger The ergs per cycle per cubic centimetre are less in the ratio 705/1030

Table II —Hysteresis

Expt	H_{max}	B_{max}	Permeability, μ	Ergs per cycle per cubic cm	Coercive force, H_0	Residual magnetism, B_0.
4	0 223	369	1655	5 53	0 0646	116
	0 471	2800	5940	215	0 306	2100
	0 726	6040	8320	705	0 404	5150
	2 77	10460	3780	1750	0 488	9020
'Roy Soc Proc,' A, vol 80, p 548 (1908)	1 354	6050	4470	1030	0 60	4666

Ring No 2

This specimen had been cooled several times to the temperature of liquid air, and it was mentioned in the earlier paper† that such treatment had the effect of increasing permeability when in a demagnetised condition It has behaved somewhat differently from Ring No 1, that is to say, when the specimen has been polarised in the shield the maximum permeability has not suffered so marked a change as might have been expected from the earlier experiments After a preliminary test (Experiment 5), as it was originally left after the cooling experiments, the ring was divested of its winding and raised to a temperature of about 800° C It was then allowed to cool in the shield without any applied magnetic force On re-winding it the permeability was found to be slightly smaller (Experiment 6) The ring was then wound with an asbestos-covered coil and allowed to cool from about 800° C in the shield, with a steady force of 14 C.G.S applied constantly. Experiment 8 was then made As in the case of Ring No 1,

* 'Roy. Soc. Proc.,' A, vol 80, p 548 (1908)
† 'Phys. Soc. Proc,' vol. 23, Part 4, p 256, June 15, 1911

a maximum permeability of over 10,000 was obtained, and it is larger than in the case of Ring No 1, for the higher values of the magnetic induction. Curve 8 can be compared with Curve 1 in this connection. The specimen was then re-wound and Experiment 9 made. The effect of mechanical disturbance has again been to lower the maximum permeability, but in this case to 7230, as against 8330 in the case of Ring No 1. After demagnetising the specimen from a force of 8 95 C G S units Experiment 10 was made. It will be seen that, although the permeability at low forces is increased, the maximum value is not diminished, as might have been expected

In each of the above cases no allowance has been made for slight possible burning away of magnetisable material

Ring No 3

In order to compare the results above described with those obtained by treatment in the shield without heating, another specimen of stalloy was chosen and as the polarising forces used in the original paper were small, it was thought well to try the effect of a larger one. Ring No 3 was polarised to a force of 174 C G S units in the shield, and Experiment 11 was then made. The maximum permeability in this specimen has the value 6900 as against 5900 in the earlier experiments. Demagnetising the specimen from $H = 2$ C G S units has increased the permeability at the lower forces but not seriously affected its maximum value. Curve 12 is interesting, as it shows that the moderate maximum permeability of 6900 gives rise to higher permeabilities at the larger values of the magnetic induction

Electric Resistance

An experiment has been made to discover whether the specific resistance of stalloy is affected when it has been subjected to cold treatment in the shield, and has yielded a negative result

Conclusion

The experiments show that the permeability of stalloy in ring form can be increased greatly by heat treatment, that is by allowing the material to cool through the temperature at which it becomes a magnetisable substance during the time that it is shielded from the influence of the earth's magnetism and subjected to a magnetising force. Values of the permeability higher than 10,000 have been obtained. A characteristic feature of the curve of permeability and magnetic induction is that the higher the maximum permeability the lower is the permeability at the higher values of the induction. The

dissipation of energy due to magnetic hysteresis is lower than in the normal stalloy specimen for a given value of the magnetic induction

The above experiments were made in the Sir William Siemens Electrical Engineering Laboratory, University of London, King's College   I wish to thank my laboratory attendant, Mr George Jones, for the assistance which he rendered

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On Newcomb's Method of Investigating Periodicities and its Application to Bruckner's Weather Cycle

By Prof ARTHUR SCHUSTER, Sec R S

(Received April 21,—Read May 7, 1914)

During the last few years of his life Prof Simon Newcomb was keenly interested in the problem of periodicities, and devised a new method for their investigation   This method is explained, and to some extent applied, in a paper entitled "A Search for Fluctuations in the Sun's Thermal Radiation through their Influence on Terrestrial Temperature" The importance of the question justifies a critical examination of the relationship of the older methods to that of Newcomb, and though I do not agree with his contention that his process gives us more than can be obtained from Fourier's analysis, it has the advantage of great simplicity in its numerical work, and should prove useful in a certain, though I am afraid, very limited field

Let $f(t)$ represent a function of a variable which we may take to be the time, and let the average value of the function be zero   Newcomb examines the sum of the series

$$f(t_1)f(t_1+\tau)+f(t_2)f(t_2+\tau)+f(t_3)f(t_3+\tau)+ . ,$$

where t_1, t_2, etc , are definite values of the variable which are taken to lie at equal distances from each other. If the function be periodic so as to repeat itself after an interval τ, the products are all squares and each term is positive   If, on the other hand, the periodic time be 2τ, each product will be negative and the sum itself therefore negative.   It is easy to see that if τ be varied continuously the sum of the series passes through maxima and minima, and the maxima will indicate the periodic time, or any of its multiples

Newcomb takes, for convenience, successive values of τ to be equal to multiples of the interval $\omega = t_{n+1} - t_n$, so that if a_1, a_2, etc, now represent the successive values of the function, it is sufficient to calculate the sums

$$\Sigma (a_n \; a_{n+1}) = a_1 a_2 + a_2 a_3 + a_3 a_4 + \; .,$$

$$\Sigma (a_n \; a_{n+2}) = a_1 a_3 + a_2 a_4 + a_3 a_5 + \; .,$$

the general term being

$$\Sigma a_n a_{n+p} = a_1 a_{p+1} + a_2 a_{p+2} + a_3 a_{p+3} + \; .$$

If the sum $\Sigma (a_n a_{n+p})$ be the first to give a maximum, a periodicity with time $p\omega$ is indicated

The relationship of Newcomb's method to that based on Fourier's analysis is easily established   Writing

$$2f(t)f(t+\tau) = [f(t)+f(t+\tau)]^2 - [f(t)]^2 - [f(t+\tau)]^2,$$

give to t successive values t_1, t_2, etc , and perform the summation   If the total range of time included be large compared to τ, the sum involving the second term of the right-hand side will be sensibly equal to the corresponding sum of the third term and independent of τ.   The variation in the value of the sum of the left-hand term, which is twice Newcomb's sum of products, depends therefore on the variation of

$$\Sigma \{f(t)+f(t+\tau)\}^2 \tag{1}$$

The interpretation of this is obvious, if we make use of the optical analogy to which I have drawn attention in previous communications.   For in any train of waves we may identify $f(t)$ with some vector such that the energy passing unit surface at that point is proportional to the integral of $[f(t)]^2 dt$ taken between the proper limits.   If in the expression (1) the sum is replaced by an integral, we see that it can be identified with the energy of two superposed equal trains of disturbances, one being retarded with reference to the other through a time interval τ, and the variation of τ gives us the interference pattern formed by a grating with only two reflecting spaces.   There is, therefore, no difference in principle between Newcomb's method and that of the periodogram, both having their analogies in the spectroscopic resolution of light, but while the periodogram aims at separating true periodicities from accidental ones by high resolving powers, Prof. Newcomb restricts the resolving power to its lowest possible value   This renders it quite ineffective as a detector of hidden periodicities. Its use, if any, must lie in a different direction

The class of problems for which Newcomb devised his method is that which contains what he calls a "tendency" towards a periodicity   As an example, he gives the fluctuation of ocean waves, or the swing of a

pendulum which is subjected, at intervals, to impulses altering its phase and amplitude, and argues that here Fourier's method might give "no period whatever" This statement is not correct In the case contemplated, the harmonic analysis would give the resultant (taking account of difference of phase) of all the Fourier terms obtained when each group of undisturbed oscillations is treated separately, such group, consisting of a limited number of oscillations, does not constitute a homogeneous system, but contains a number of periods adjacent to the principal one The resultant of the combined groups for each period can be estimated by applying a theorem due to Lord Rayleigh,* which reduces the question to one of probabilities. According to this theorem, there is a definite expectancy for the resultant amplitude, which can be expressed in a simple manner, if the amplitudes due to separate groups are equal In that case, the expectancy for the resultant is $\sqrt{n}$ times the common amplitude, if n be the number of groups, and although it may happen that for one period the resultant is zero, this is compensated by amplitudes greater than the expectancy in the adjacent periods, the average for all these periods being perfectly definite In the periodogram method the average intensity is taken for closely adjoining frequencies, and this avoids all ambiguity or possibility of failure

In optical language, the disturbance contemplated by Newcomb has a spectrum containing one band which may be broad if the number of undisturbed oscillations be small For a spectrum of this kind small resolving powers may be as good as large ones, and much better if account be taken of the diminution of labour involved But in cases such as occur most frequently, we must be careful to remember that what may look like a single broad band may really be a superposition of several bands which the low power is not capable of resolving We should therefore use the method of low resolving powers cautiously, as a first exploration, to see what kind of disturbance we are dealing with For definite periods standing out feebly against a continuous background high powers are essential

There is one distinction between an optical or acoustical train of waves and the disturbances which are contemplated in the present discussion. In the former cases we have no knowledge of the actual displacements and the separation of periods by optical analysis or by resonance is the only method available In hunting for periodicities in cosmical phenomena we start on the other hand with a direct knowledge of the vector to be analysed, and it might be urged that this additional source of information allows us to apply a more direct treatment than that based on Fourier's analysis. My reply is

* "On the Resultant of a Number of Vibrations of the same Pitch and Arbitrary Phase," 'Phil. Mag,' vol. 10, p 73 (1880).

that in the cases which I have mainly had in view, the additional information is of no assistance, the periodicities to be looked for being hidden by accidental or at any rate irregular disturbances   There are, however, intermediate cases between obvious periods, such as the diurnal change of temperature, and hidden periods such as that involved in the possible synchronism of sunspots and meteorological phenomena   A case in point is the sunspot curve   A period in the neighbourhood of eleven years is clearly indicated without recourse to analysis, by direct inspection of the variations and the number of spots, but the regular cycle is interfered with and considerable variations in the distances between successive maxima are observed   Fourier's analysis here may possibly be supplemented by other investigations, though it cannot be replaced by them   When, however, the curve of variability gives us no indication by direct inspection of the periodicity looked for, the periodogram method seems to me to be the only available one

About 25 years ago, Dr Eduard Bruckner, investigating secular changes of climate, came to the conclusion that "the variations of climate consist of fluctuations of temperature, barometric pressure and rainfall, which occur simultaneously over the whole earth in a period of 35 years."   Examining the evidence on which this very definite conclusion is based, it occurred to me that the periodicity claimed—if it has a reality—must be of the kind for which Newcomb's* method is specially applicable   The average distances between successive maxima or minima in the series of observations on which Bruckner bases his conclusions vary very considerably, and though there can be no question of a strict period, there seemed sufficient evidence of *groups* of periods near 35 years to render further investigation desirable   In the meantime meteorologists generally have accepted Bruckner's cycle, and sometimes used it as a basis for predicting a succession of cold or warm winters.

The records collected by Brückner for the frequency of exceptionally cold winters date back to the year 800 and are summarised in a table in which progressively from 5 to 5 years the numbers of these winters in an interval of 20 years are given   Thus the figure attached to the year 1430 represents the number of cold winters between 1420 and 1440, and the next figure attached to the year 1435 is the number of cold winters in the interval 1425 to 1445   It is clear that this process eliminates any period of 20 years or of its submultiples, and considerably diminishes the amplitude of periodicities up to 25 or 30 years

In applying Newcomb's procedure to Brückner's series of figures, I have formed the summation of the products $\sum_{n=0}^{n=t} a_n . a_{n+p}$, increasing the values of p

from 1 to 14, the periods examined are therefore the 14 first multiples of 5 years. The whole series of data was divided into ten sets each extending over 100 years.

The summation is performed for each set by giving the appropriate values to s and t. In the first series of sums s is put equal to 1 and t equal to 19; in the second series the limits would be 20 and 29. We obtain in this way nine complete sets of sums, which are given in Table I. The summation of the vertical columns gives the final result, subject to a correction due to the divergence of the mean value of a from zero. This correction consists mainly of a constant to be subtracted, and might therefore be neglected, as we have only to consider the fluctuations in the value of Newcomb's sums, but there is a small outstanding difference which in the present case is appreciable, because, owing, no doubt, to the better statistical information, the number of cold winters in Bruckner's table is considerably greater at the end than it was at the beginning of the series. To determine the correction, let c be the general average of all the values of a, and let m be their total number, so that $mc = \Sigma a_n$. We have then —

$$\Sigma (a_n - c)(a_{n+p} - c) = \Sigma a_n a_{n+p} - m^{-1} \Sigma a_n \Sigma a_{n+p}$$

The summation is to be taken from $n = 1$ to $n = m$.

If in the last term we substitute

$$\Sigma a_{n+p} - \Sigma a_n = (a_{m+1} - a_1) + (a_{m+2} - a_2) + \quad + (a_{m+p} - a_p), \qquad (2)$$

Table I.—Records of Cold Winters from the Year 800 ($n = 1$) to 1775 ($n = 195$).

	$n = s + 19$ $\Sigma\ a_n a_{n+p}$ $n = s$ (Period in years = $5p$)														
$5p$	0	5	10	15	20.	25	30	35	40	45	50	55	60	65	70
$s = 1$	114	106	97	89	82	80	77	78	81	90	101	106	104	96	90
$s = 21$	116	120	107	105	93	90	81	68	66	78	95	115	126	139	146
$s = 41$	264	251	240	234	240	258	275	293	314	334	359	369	375	374	373
$s = 61$	677	560	540	524	502	496	489	478	479	471	463	448	441	418
$s = 81$	549	550	540	536	529	519	513	501	496	499	508	509	530	545	567
$s = 101$	548	510	486	452	434	431	446	463	482	497	485	471	452	434	425
$s = 121$	444	402	381	353	323	334	315	315	300	283	285	280	295	340	342
$s = 141$	465	453	487	511	531	551	553	557	547	543	550	580	589	608	617
$s = 161$	916	884	819	735	664	664	685	735	762	753	738	651	605	569	572
Sum ..	4093	3836	3697	3539	3396	3418	3434	3895	3526	3556	3587	3544	3524	3538	3550
Newcomb's periodogram	318	636	493	326	177	188	202	144	259	276	290	243	227	237	249

We see that the correction to be applied to $\Sigma a_n \Sigma a_{n+p}$ to reduce it to the value it would have if all quantities a were referred to their common average consists of a constant term $m^{-1}(\Sigma a_n)^2$, and a term depending on p which is m^{-1} times that standing on the right-hand side of equation (2), both corrections are to be subtracted   Newcomb's sums corrected in this fashion are given in the last row of the Tables, and this row of figures may be called " Newcomb's periodogram "

Before discussing the conclusions to be drawn from the records of cold winters, I take as a second example the dates of the beginning of the vintage in Central Europe, for which we possess records dating back to the Middle Ages   These, so far as they relate to France, have been collected with great care by Angot, and similar information referring to parts of Germany and Switzerland is available, and was used by Brückner   Without describing the method which he has used in order to eliminate local peculiarities and obtain a homogeneous series, it is sufficient to say that the figures he used are five years' averages, the smaller numbers indicating late vintages   Table II gives the results arranged as in Table I

Table II —Records of Vintages for each Lustrum from 1496-1500 ($n = 1$)
to 1881-1885 ($n = 74$)

		$n = s + p$ $\Sigma\, a_n \;\; a_{n+p}$ $n = s$													
$5p$	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
$s = 1$	2729	2106	1949	2361	2269	2190	2220	2286	2045	2087	2524	2337	2212	2452	2254
$s = 21$	2884	2488	2364	2412	2430	2405	2241	2144	2228	2105	2026	1608	1798	1814	1844
$s = 41$	1287	1059	1061	1042	1114	1004	1046	1002	974	1041	1101	1129	961	1076	1132
Sum	6900	5653	5374	5815	5813	5599	5507	5432	5247	5233	5651	5074	4986	5342	5230
Newcomb's periodogram	1236	29	−193	296	294	167	211	117	−53	−61	424	108	−193	250	80

In interpreting the results of these tables we must bear in mind that Newcomb's periodogram depends on a single retardation, and corresponds to the analysis of light by two slits   Consequently we have not only the " central image," but an overlapping of spectra, showing maxima for retardations equal to zero or to any multiple of the original period.   The central image is indicated in the tables by the high value of the initial column corresponding to zero retardation.   The minimum in the record of cold

winters which is shown with a period of 20 years is obviously due to the method of treating the observations by taking averages over 20 years, and hence eliminating any real or accidental period of 20 years   The records of vintages show a maximum for a period somewhere between 15 and 20 years, and a minimum for a period of 10 years.   This indicates that there is no prominent period of smaller time than 15 years   (A negative number means an intensity diminished by interference, and if there is a period τ, negative numbers should therefore appear for a retardation $\frac{1}{2}\tau$)   Both Tables indicate a maximum for a period of 50 years, and neither of them gives any indication of Bruckner's cycle of 35 years, though both records agree in a very small rise for a period of 30 years   The maximum of 50 years which is so well marked in the vintage records is found on applying Fourier's analysis to be due to a periodicity of 25 years, and the minor maximum at 30 years is similarly due to the periodicity of 15 years   Supplementing Newcomb's analysis by the usual process, I can find no evidence of a definite period, except possibly that of 15 years

The main conclusions of the present enquiry are—

1   Newcomb's method of investigating periodicities is only applicable to special cases, the results obtained being in general difficult to interpret

2   Newcomb's method when applied to Brückner's 35 years' weather cycle does not lend any support to the reality of that cycle, although it seems specially adapted to deal with the type of periodic fluctuations which are advocated by Bruckner

To prevent misunderstandings it seems advisable to point out that Bruckner's conclusions as to fluctuations of climate extending over long periods of years and affecting simultaneously a large part of the earth are not affected by the above results   I consider them, on the contrary, to be of great importance, although in my opinion no periodicity in the proper sense of the term has been established

On the Effect of the Magneton in the Scattering of α-Rays.

By W. M. Hicks, Sc.D., F.R.S.

The present communication is intended to illustrate a remark made in the discussion on the constitution of the atom at the meeting of the Society on March 19. Its object is no more than to show that the molecular magnetic fields discovered by Weiss are very efficient agents in the scattering of α- and β-particles. For this purpose the simple case of charged particles moving in the equatorial plane of a fixed magnetic doublet is considered without taking account of a central nuclear charge. The solution of this simple problem will be sufficient to enable a rough estimate of the magnitude of the effect to be formed.

Suppose the plane of the paper to be the equatorial plane of the doublet situated at O (figs 1, 2) with its north pole above the paper so that the field is down through the paper and is equal to M/r^3.

Fig. 1

Fig. 2
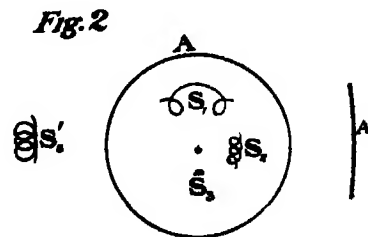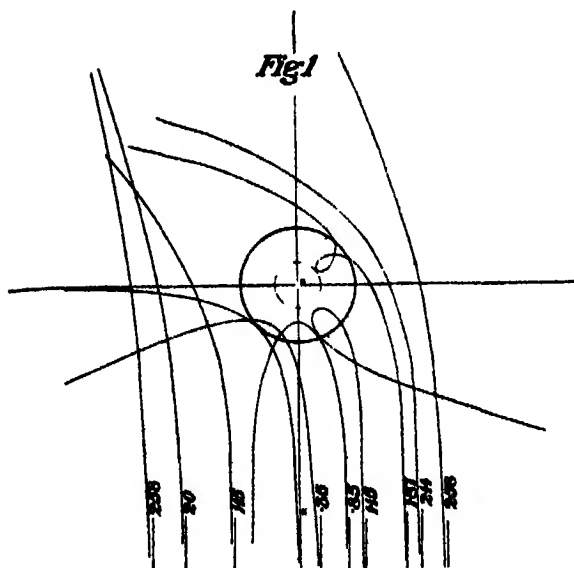
Suppose the particles at a great distance are moving parallel to XO. The paths will all be curved, with their concavities on the left of the direction of motion. Further, let e denote the charge in magnetic units, m the mass, and v the velocity. Then the force normal to the path

$$= Hev = \frac{mv^2}{\rho},$$

where ρ is the radius of curvature.

Hence
$$\rho = \frac{mv}{e\mathrm{H}} = \frac{mv}{e\mathrm{M}} \quad r^3 = \frac{r^3}{a^2},$$

where $a = \sqrt{\dfrac{e\mathrm{M}}{mv}}$ and is of the dimensions of a length

Two cases arise according as the path is (1) convex or (11) concave to O. If p denote the perpendicular from O on the tangent,

$$r\frac{dr}{dp} = -\rho \quad \text{in Case 1,}$$
$$= +\rho \quad \text{in Case 11}$$

Hence
$$\rho = \mathrm{C} + \frac{a^2}{r}, \quad \text{Case 1,}$$
$$= \mathrm{C} - \frac{a^2}{r}, \quad \text{Case 11}$$

In the paths of special interest for our present purpose the particles arrive from infinity If p' denote the distance of the particles from the line XO at a great distance, $\mathrm{C} = p'$ It will be convenient to write $p' = 2a\tan\alpha$, so that all values of p' will be contained between $\alpha = 0$ and $\pi/2$, also to put $1/r = u$

Then $p = 2a\tan\alpha \pm a^2 u$ according to Case 1 or 11 The possible apsidal distances are found by putting $p = r$, and are therefore given by

Case 1

Case 11

$$1 = 2au\tan\alpha + a^2 u^2, \qquad 1 = 2au\tan\alpha - a^2 u^2,$$

or
$$au = \frac{1 - \sin\alpha}{\cos\alpha}, \qquad au = \frac{\sin\alpha \pm \sqrt{(\sin^2\alpha - \cos^2\alpha)}}{\cos\alpha}$$
$$= \text{imaginary when } \alpha < \pi/4$$

Also when there are tangents to the orbits from O, their lengths are found by putting $p = 0$, or

$$\text{Length of tangent} = a^2/p' = \tfrac{1}{2}a\cot\alpha \text{ in Case 11.}$$

It is interesting to notice that there is no dynamical reversibility here. If, say at an apse, the velocity of a particle is reversed, the particle does not return over its former path, because the forces are also reversed Nevertheless the actual path is clearly symmetrical on the two sides of an apse *

Using polar co-ordinates with XO for the initial line,

$$p = r^2\frac{d\theta}{ds},$$

$$\frac{dr}{d\theta} = \pm \frac{r\sqrt{(r^2 - p^2)}}{p}$$

* If the forces between the molecules in a gas depend on magnetic fields, the paths will not be reversible, and a difficulty felt in the kinetic theory of gases will be obviated.

Case i.—Particles projected on left of OX.

$$p = 2a \tan \alpha + a^2 u$$

Before an apse is reached $dr/d\theta$ is negative

$$\frac{du}{d\theta} = \frac{\sqrt{\{1-(2aut+a^2u^2)^2\}}}{2at+a^2u},$$

where t stands for $\tan \alpha$

Hence the equation to the path is

$$\theta = \int_0^u \frac{2at+a^2u}{\sqrt{\{1-(2aut+a^2u^2)^2\}}} du$$

$$= \tfrac{1}{2} \sin^{-1}(2aut+a^2u) + at \int_0^u \frac{du}{\sqrt{\{1-(2aut+a^2u^2)^2\}}}$$

To transform the elliptic integral write $2aut+a^2u^2 = \cos \chi$

$$\text{The int} = \tfrac{1}{2} t \int_\chi^{\pi/2} \frac{d\chi}{\sqrt{(t^2+\cos \chi)}} = \sin \alpha \int_\chi^{\pi/2} \frac{d(\chi/2)}{\sqrt{\{1-k^2 \sin^2(\chi/2)\}}},$$

where $k = \sqrt{2} \cos \alpha$ This is, therefore, suitable for $\cos \alpha < 1/\sqrt{2}$ or $\alpha > \pi/4$, $i.e.$, $p' > 2a$.

Hence, when $p' > 2a$,

$$\theta = \tfrac{1}{2} \sin^{-1}(2aut+a^2u) + \sin \alpha \int_\phi^{\pi/4} \frac{d\phi}{\sqrt{(1-k^2 \sin^2 \phi)}},$$

where $\cos 2\phi = \cos \chi = 2aut+a^2u^2$

and $\sin \phi = \sqrt{\left\{\dfrac{1-2aut-a^2u^2}{2}\right\}},$

When $p' < 2a$ write $\lambda \sin \phi = \sin \theta$ and replace θ by ϕ

$$\theta = \tfrac{1}{2} \sin^{-1}(2aut+a^2u) + \frac{1}{\sqrt{2}} \tan \alpha \int_\phi^{\pi/2-\alpha} \frac{d\phi}{\sqrt{(1-\lambda^2 \sin^2 \phi)}},$$

with $\lambda = \dfrac{1}{\sqrt{2} \cos \alpha} = \dfrac{1}{k}$ and $\sin \phi = \cos \alpha \sqrt{\{1-2aut-a^2u^2\}}$

For particles aimed to the left of XO, therefore—

When $p' > 2a$—

   Apsidal angle $= \Theta = \dfrac{\pi}{4} + \sin \alpha\, F\left(k \cdot \dfrac{\pi}{4}\right),$

   Apsidal distance $= a \dfrac{1+\sin \alpha}{\cos \alpha}$

When $p' < 2a$—

   Apsidal angle $= \Theta = \dfrac{\pi}{4} + \dfrac{1}{\sqrt{2}} \tan \alpha\, F\left(\lambda \cdot \dfrac{\pi}{2} - \alpha\right),$

   Apsidal distance $= a \dfrac{1+\sin \alpha}{\cos \alpha}$

For a particle shot along XO, $p' = 0$, $\alpha = 0$

$$\theta = \tfrac{1}{2}\sin^{-1}a^2u^2,$$

or

$$a^2u^2 = \sin 2\theta,$$

a rectangular hyperbola   The deflection is therefore 90°

For a particle shot at a distance $2a$, $k = \lambda = 1$

$$\theta = \tfrac{1}{2}\left(\frac{\pi}{2} - 2\phi\right) + \frac{1}{2\sqrt{2}}\log_e(3 + \sqrt{2})\frac{1 - \sin\phi}{1 + \sin\phi},$$

with

$$\sin\phi = \sqrt{\left\{\frac{1 - 2uu - a^2u^2}{2}\right\}}$$

The deflection is $\dfrac{\pi}{2} - \dfrac{1}{\sqrt{2}}\log_e(3 + 2\sqrt{2}) = 18° \ 35'$,

with apsidal distance $a(\sqrt{2} + 1) = 2\,414a$

The particles coming in on the left of XO are therefore scattered within a right angle and none are reflected

Case II.—Particles shot on right of XO.

Here $p = p' - a^2/r = 2at - a^4u$

As in Case 1,

$$\theta = \tfrac{1}{2}\sin^{-1}(2aut - a^2u^2) + at\int_0^u \frac{du}{\sqrt{\{1 - (2aut - a^2u^2)^2\}}}$$

When $p' < 2a$ or $\alpha < \pi/4$ there is no apse, and au increases from 0 until at $au = 2t$, $p = 0$, or the radius vector touches the orbit   Beyond this the path is convex to O.   Let θ_1 denote the angle up to the tangent   The argument of the $\sin^{-1}$ term increases from 0 to a maximum value t_2, and then decreases to 0   Hence between the limits the value is 0.   So the integral between the same limits is

$$2at\int_0^{t/a} \frac{du}{\sqrt{\{1 - (2aut - a^2u^2)^2\}}},$$

or, with the same notation as before,

$$\frac{2}{\sqrt{2}}t\int_{\phi_2}^{\phi_1} \frac{d\phi}{\sqrt{\{1 - \lambda^2\sin^2\phi\}}},$$

with

$$\lambda = \frac{1}{\sqrt{2}\cos\alpha}.$$

$$\sin\phi = \cos\alpha\sqrt{(1 + 2aut - a^2u^2)} = \sqrt{\{1 - (\sin\alpha - au\cos\alpha)^2\}},$$

hence $\sin\phi_1 = \cos\alpha = \sin\left(\dfrac{\pi}{2} - \alpha\right)$ or $\phi_1 = \dfrac{\pi}{2} - \alpha$,

also ϕ_2 corresponds to $au = t$

$$\sin\phi_2 = 1.$$

Therefore

$$\theta_1 = \sqrt{2}\tan\alpha \int_{\pi/2-\alpha}^{\pi/2} \frac{d\phi}{\sqrt{(1-\lambda^2\sin^2\phi)}} = \sqrt{2}\tan\alpha\left\{F\left(\lambda.\frac{\pi}{2}\right)-F\left(\lambda\;\frac{\pi}{2}-\alpha\right)\right\}.$$

Beyond the tangent point

$$p = a^2u - 2a\tan\alpha,$$

and there is now an apse at

$$au = \frac{1+\sin\alpha}{\cos\alpha}$$

Also $dr/d\theta$ is now positive and

$$\frac{du}{d\theta} = -\frac{\sqrt{\{1-(a^2u^2-2aut)^2\}}}{a^2u-2at}$$

$$\theta = -\tfrac{1}{2}\sin^{-1}(a^2u^2-2aut)+at\int\frac{du}{\sqrt{\{1-(a^2u^2-2aut)^2\}}}$$

As in Case 1, transform the integral by writing $a^2u^2-2aut = \cos 2\chi$, and $k\sin\chi = \sin\phi$, giving

$$\sin\phi = \cos\alpha\sqrt{\{1+2aut-a^2u^2\}}.$$

To $au = 2t$ corresponds

$$\sin\phi = \cos\alpha \quad\text{or}\quad \phi = \frac{\pi}{2}-\alpha$$

To the apse corresponds

$$\sin\phi = 0 \qquad\text{,,}\qquad \phi = 0$$

If then θ_2 denote the angle from tangent to apse,

$$\theta_2 = -\tfrac{1}{2}\sin^{-1}(1)+\frac{1}{\sqrt{2}}\tan\alpha\int_0^{\pi/2-\alpha}\frac{d\phi}{\sqrt{\{1-\lambda^2\sin^2\phi\}}}$$

$$= -\frac{\pi}{4}+\frac{1}{\sqrt{2}}\tan\alpha\,F\left(\lambda\;\frac{\pi}{2}-\alpha\right).$$

The angle to the apse is

$$\Theta = \theta_1+\theta_2 = -\frac{\pi}{4}+\frac{1}{\sqrt{2}}\tan\alpha\left\{2F\left(\lambda.\frac{\pi}{2}\right)-F\left(\lambda\;\frac{\pi}{2}-\alpha\right)\right\}$$

When $p > 2a$ there are two possible apsidal distances since $\alpha > \pi/4$ For particles coming from infinity, u will increase from 0 and will reach the smaller value first This is therefore the apsidal value for our immediate purpose, and

$$au = \frac{\sin\alpha-\sqrt{(\sin^2\alpha-\cos^2\alpha)}}{\cos\alpha}.$$

We have $\quad \theta = \frac{1}{2}\sin^{-1}(2aut - a^2u^2) + \sin\alpha \displaystyle\int_{\pi/4}^{\phi}\frac{d\phi}{\sqrt{\{1 - k^2\sin^2\phi\}}}$,

with $\qquad\qquad\qquad\qquad k = \sqrt{2}\cos\alpha$

$$\sin\phi = \sqrt{\frac{1 + 2aut - a^2u^2}{2}} = \sqrt{\{1 - \tfrac{1}{2}(1 - 2aut + a^2u^2)\}}$$

$$= \sqrt{\{1 - \tfrac{1}{2}(au - q_1)(au - q_2)\}},$$

where q_1, q_2 are the two roots of the apsidal equation, $q_1 < q_2$. Since $(au - q_1)(au - q_2)$ must be positive, $au < q_1$ or $> q_2$.

Now $au = q_1 = t - \sqrt{(t^2 - 1)}$, whereas the possible tangents are given by $au = 2t$. Hence au is always less than a possible tangent, or, in other words, the orbits are all concave to O.

As au increases from 0 to q_1, ϕ increases from $\pi/4$ to $\pi/2$. Hence the apsidal angle is

$$\Theta = \frac{\pi}{4} + \sin\alpha\left\{F\left(k, \frac{\pi}{2}\right) - F\left(k, \frac{\pi}{4}\right)\right\}, \qquad k = \sqrt{2}\cos\alpha$$

Scrolls.—Although not required for the immediate purpose of this paper, it may be interesting to complete the theory of the orbits by considering the case of those orbits which do not stretch to infinity. It is the case where au is greater than the root q_2 in the immediately preceding paragraph, or

$$au \gtreqqless t + \sqrt{(t^2 - 1)},$$

with $\qquad\qquad\qquad\qquad t > 1 \quad \text{or} \quad \alpha > \pi/4$

$$\theta = \frac{1}{2}\sin^{-1}(2aut - a^2u^2) + \sin\alpha\int_{\pi/4}^{\phi}\frac{d\phi}{\sqrt{(1 - k^2\sin^2\phi)}},$$

with

$k = \sqrt{2}\cos\alpha$ and $\sin\phi = \sqrt{\dfrac{1 + 2aut - a^2u^2}{2}} = \sqrt{\{1 - \tfrac{1}{2}(1 - 2aut + a^2u^2)\}}$

Since ϕ is real,

$$1 + 2aut - a^2u^2 > 0,$$

$$au \gtreqqless t + \sqrt{(t^2 + 1)} \gtreqqless \frac{1 + \sin\alpha}{\cos\alpha}.$$

Thus au lies between $t + \sqrt{(t^2 - 1)}$ and $t + \sqrt{(t^2 + 1)}$. As au increases from the smaller value it passes through the value $2t$, corresponding to a tangent through O, and, as in the former cases, the curve changes into one convex to O. In the concave part the amplitude of the integral increases from $\phi = \pi/2$ to $\phi = \pi - \pi/4$, and the angular distance from apse to tangent is

$$\theta_1 = \frac{1}{2}\left(0 - \frac{\pi}{2}\right) + \sin\alpha\int_{\pi/2}^{\pi - \pi/4}\frac{d\phi}{\sqrt{(1 - k^2\sin^2\phi)}}$$

$$= -\frac{\pi}{4} + \sin\alpha\left\{F\left(k, \frac{\pi}{2}\right) - F\left(k, \frac{\pi}{4}\right)\right\}.$$

The curve now changes   The apsidal distance is given by

$$a^2u^2 - 2aut = 1, \qquad au = \frac{1+\sin\alpha}{\cos\alpha}$$

$dr/d\theta$ is $+$ and $\qquad \dfrac{du}{d\theta} = -\dfrac{\sqrt{\{1-(a^2u^2-2aut)^2\}}}{a^2u^2-2aut}.$

$$\theta = -\sin^{-1}(a^2u^2 - 2aut) + at\int \frac{du}{\sqrt{\{1-(a^2u^2-2aut)\}}}$$

$$= -\sin^{-1}(a^2u^2 - 2aut) + \sin\alpha\int_\phi^{\pi/4} \frac{d\phi}{\sqrt{(1-k^2\sin^2\phi)}}$$

As au goes from $2t$ to the apse ϕ goes down from $\pi/4$ to 0

$$\theta_2 = -\frac{\pi}{4} + \sin\alpha\, \mathrm{F}\left(k\ \frac{\pi}{4}\right),$$

$$\Theta = \theta_1 + \theta_2 = \sin\alpha\, \mathrm{F}\left(k\ \frac{\pi}{2}\right) - \frac{\pi}{2}$$

It is now easy to see the general arrangement of the orbits   The change of shape, according as the shot is aimed at different distances from O, is illustrated in fig 1.   Shots on the left of O are all deflected to the left between 0° and 90°.   None are reflected back   That aimed directly at O describes a rectangular hyperbola, touching the circle radius $= a$ With increasing distances on the right of O, the particles are first reflected in a backward direction in paths of the general appearance of hyperbolas That aimed about $0.85a$ on the right is returned in the opposite direction Farther off the return path crosses the incident, and loops are produced. The most remarkable effect is when the aim is very close to $p = 2a$ Just less than this the path is a spiral of very many turns, then a loop, and the same number of turns in getting free   Just greater than $2a$, the paths are also spirals with many turns, but in this case coming to an apse without a loop, and then getting free.   This critical circle is the path we should obtain if we proceeded to calculate the circular orbit in the usual direct way

It is therefore clear that this orbit is unstable.   All particles aimed within a small distance $\pm dp$ of $2a$ on the right will be scattered in all directions, but the total number through dp is so small that this effect would have little influence on the law of scattering   To deduce a law of scattering it would be advantageous to calculate the deflections for equal intervals of p' There is, however, no object to be gained by doing so, as the result can scarcely correspond to reality, for two reasons.   First, because the theory is not complete as dealing with particles moving in the equatorial plane only; and, secondly, because in the case of α- and β-particles, the electric reactions

are not considered * A theory which neglects the electrostatic forces is as deficient as one which neglects the magneton effect In the figures, therefore, orbits only have been calculated for selected values of λ and λ which occur in the tables of elliptic integrals given in Bertrand's 'Integral Calculus'

It is interesting to note that a particle moving in an orbit sufficiently close to the circle (radius $= a$) behaves like a radioactive α- or β-particle By taking it close enough, it may be arranged to describe any number of revolutions, *i.e*, have any life, and then disintegrate

Scrolls

A_2, A_1 denote the maximum and minimum apsidal distances respectively

A_2/a	A_1/a	tang/a	θ_1		θ_2	
			° ′		° ′	
0 6897	0 3945	0 4673	84 20		−8 19	
0 4742	0 3419	0 3871	14 8		−6 27	
0 3179	0 2680	0 2887	6 1		−4 1	
0 1962	0 1826	0 1889	2 15		−1 53	
0 0940	0 0924	0 0931	0 30		−0 29	
0 ·0622	0 ·0616	0 0618	0 13		−0 13	

Orbits from Infinity

	Left of O			Right of O			
$p'/2a$	θ	apse/a	θ	θ_2	apse/a	tang/a
	° ′		° ′	° ′		
8 086	89 47	16 233	90 13		16 110	
5 ·369	89 31	10 831	90 30		10 645	
2 646	88 7	5 475	92 15		5 097	
1 732	85 59	3 ·732	96 1		3 146	
1 291	88 33	2 ·925	104 8		2 109	
1 070	81 31	2 534	124 20		1 450	
1 ·000	80 42	2 414	∞		1 000	
0 9996	80 42	2 ·4136	359 32	9 18	0 414	0 500
0 ·969	80 19	2 ·361	167 17	9 41	0 423	0 516
0 ·930	79 47	2 296	128 52	10 13	0 434	0 587
0 707	75 53	1 932	47 40	14 7	0 517	0 707
0 ·649	74 36	1 842	35 28	15 24	0 542	0 ·770
0 577	72 47	1 ·732	22 16	17 13	0 577	0 866
0 424	68 0	1 ·510	− 1 39	22 0	0 662	1 178
0 176	56 34	1 192	−29 53	33 26	0 839	2 835
0	45 0	1 ·000	−45 0	45 0	1 ·000	∞

Fig 2 illustrates a few of the scroll orbits The inner apse always lies within a circle whose radius is $(\sqrt{2}-1)a$, the outer apse within the critical circle a The scroll S_2 is so small that an enlarged drawing is given on the

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* This case admits of treatment similar to that here given, but the discussion of the elliptic integral involved is more complicated. I hope to return to this on a later occasion.

same figure magnified five times, O', A', S'₃, corresponding to O, A, S₃. It is curious to note that a particle takes much longer to make one revolution round O than if it circulated directly with its special velocity v. When close in the loops become almost close circles For instance, for a distance about 0 09a, each loop is displaced about 1 minute from the preceding one, and its radius is 0 0016a It would take 192 times as long When very close in it would appear almost stationary, with a sort of secular change of position

Of the particles from outside none can penetrate nearer to O than $(\sqrt{2}-1)a$ If we take the case of a single magneton $M = 1\ 6 \times 10^{-21}$ For a β-particle $e/m = 1\ 73 \times 10^7$ and $v = 10^{10}$ about For an α-particle we may take e/mv about $2\ 5 \times 10^{-6}$ Consequently

$$a = 1\ 6 \times 10^{-12} \text{ for a } \beta\text{-particle,}$$
$$a = 0\ 6 \times 13^{-13} \text{ for an } \alpha\text{-particle}$$

The nearest approach is consequently of the orders 6×10^{-13} and 2×10^{-14} for penetrating β- and α-rays respectively When the electrostatic action is taken into account the effect on the α-particle will be to make this minimum distance very much larger, not only on account of the direct action, but because the diminution of velocity caused by it will also render it more subservient to the magnetic field

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Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.—I

By the Hon R J STRUTT, Sc D, F R S, Professor of Physics, Imperial College, South Kensington.

§ 1 Introduction

In a paper entitled "Duration of Luminosity of Electric Discharge in Gases and Vapours,"[*] reference was made to a known phenomenon shown by the mercury arc *in vacuo* when mercury is allowed to distil away from a mercury lamp into a lateral tube sealed on to it, the rapidly moving vapour carries its luminosity for a long distance out of the electric field It was shown how effects not essentially different might be obtained with mercury, and other metals also, using not the arc, but the leyden jar spark between poles of the metal, but this method, owing to

* 'Roy Soc Soc,' A, vol 88, p. 110 (1913).

the intermittence of the sparks and the small scale of the effects, is far less satisfactory than the use of the arc At the time of writing the paper cited, I thought that it would be very difficult to extend the use of the arc to metals less volatile than mercury, but the problem has proved more tractable than was expected

§ 2 *Method of Experimenting—Apparatus used*

The vessel in which the arc is confined will be called, for convenience, a lamp, though it is not used directly as a source of light.

The lamp, then, containing the metal under investigation, stands in a large exhausted receiver *a* (fig 1)   It consists of a short length of rough quartz tubing* *b*, which may conveniently be from 5 to 10 cm long and 8 to 20 mm diameter   This is covered with asbestos paper, for opacity, and closed at the bottom by an asbestos stopper *c*   The latter is held
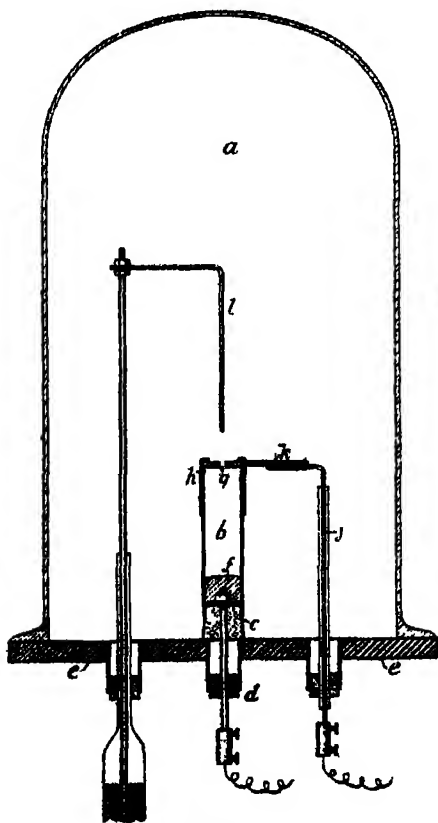

Fig. 1.

Fig 2.

* The cheap kind made by the Thermal Syndicate, Newcastle.

down by an iron stud and nut with washer The stud passes out through a rubber cork *d* which insulates it from the base plate *ee*

On the nut, and in electrical contact with it, is placed a piece of the metal under investigation—a rough lump, or, preferably, a short length of rod, of such size as to fit the quartz tube In any case enough metal should be used to form a layer 1 cm. deep over the top of the nut * In experiments with potassium and sodium a hollow iron cup replaces the nut This cup contains the alkali metal, and protects the quartz and asbestos from contact with it

The pool of metal *f* at the bottom of the lamp, melted by the heat of the arc, forms the cathode In some experiments the lamp is closed at the top by an iron diaphragm *g*, which serves as anode, and which is pierced with a central hole from which the luminous vapour issues into the space above, *g* is held down by the iron cap *h* fitted tight on to the quartz tube with asbestos paper In other experiments a cylindrical iron plug with a hole along the axis is used as anode It fits close into the tube (fig 2), and becomes hot enough in use to prevent any condensation of metal in the channel

In either case contact is made with the anode by means of a metal rod *j* passing through a rubber cork inserted in a tubulure in the air pump plate The wire ligature *k* facilitates dismounting. An iron rod *l* is provided which can be inserted into the lamp through the aperture at the top, making temporary contact between cathode and anode On withdrawing it the arc is struck , *l* can be manipulated from outside by means of an iron rod passing out through a barometric column. After the arc has been struck *l* can be turned aside out of the way

In the sectional diagram (fig 1) only two apertures through the base plate are shown, exclusive of that in the middle In all, however, there are six, equally spaced on a circle concentric with the plate. Of the remaining four, the *first* carries a brass tube of 2 cm. diameter for connection to the Gaede molecular pump, which maintains a cathode ray vacuum in the apparatus †

The *second* carries a discharge tube, with a stopcock opening to the air The state of the vacuum in the bell jar can be judged at any time by the appearance of an induction coil discharge in this tube.

The *third* and *fourth* carry vertical metal pillars, passing in through rubber

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* In some experiments with magnesium a charge of as much as 7 grm. of the metal has been distilled away

† A short rubber connection is necessary to give flexibility, and easily allows of a high enough exhaustion. A spiral spring inside keeps it from collapse.

stoppers, with ebonite bushes to support and insulate them in the tubulures passing through the plate   These serve to carry the supplementary electrodes to be mentioned later, for experimenting on the properties of the glow in an electric field

In use, the bell jar very soon becomes covered inside with an opaque deposit of volatilised metal, sometimes thick enough to peel off in a coherent film   This, of course, prevents observation of what is going on inside   The difficulty has been almost completely overcome by placing a metal tube in the bell jar, pointing at the lamp with one end close up against the glass   In this way a window corresponding to the cross section of the tube is preserved clear, the tube itself taking the deposit. The tube used is of rectangular section, 5 × 1 cm , and 5 cm long   The top of the lamp, and the space some centimetres above it, is open to observation through the window   The current usually passed is from 4 to 10 ampères   An electro-magnet in the lamp circuit to provide inductance overcomes, to a great extent, the tendency of the arc to go out   This device has been used by Lord Rayleigh

* In these experiments it was necessary to remove the bell jar, for cleaning it and for recharging the lamp with metal, two or three times in a day's work, and many scores of times in all   This has made worth while an improvement in the method of cementing it Ordinary soft red wax is used, but it is squeezed mechanically into a thread or wire 2 mm in diameter, which is laid round the flange of the bell-jar   The latter is placed on the plate without heat, and the air-pump started   The atmospheric pressure forces the bell-jar down and flattens out the wax between it and the plate, making a perfect joint   The arrangement for making the wax thread consists simply of a stopped brass tube, *a* (fig 3), with a brass plunger, *b*, fitting into it   It is placed endwise in a large
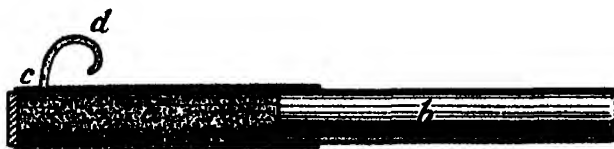
Fig 3.

parallel vice, which serves to force in the plunger   The wax thread, *d*, then exudes through a small side hole, *c*, of appropriate size, near the closed end of the cylinder

Whether the anode should take the form of a perforated diaphragm or a perforated plug depends on circumstances.   The latter has the advantage in point of durability, but when the metal to be volatilised is one which gives a luminous jet with difficulty, the diaphragm form must be used, as allowing the vapour to issue in the minimum time   An objection to it is that in some cases there is a tendency for a discharge to pass from the

outside face of the anode through the aperture and down to the cathode This is, of course, to be avoided, as the object is to examine the luminous vapour outside the region of discharge   A sheet of mica with a hole corresponding to that in the diaphragm can be placed over it, and successfully cures the trouble
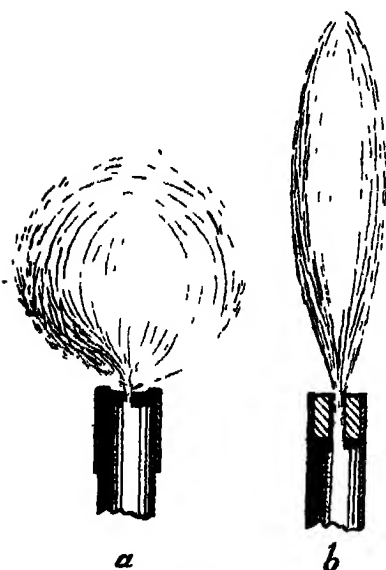
As might be expected, the shape of the issuing jet of luminous vapour depends on what kind of hole it comes out from With a hole in a thin diaphragm, the exuded vapour expands into a bulbous form (a, fig 4), with the plug form of anode, which has a long narrow channel, the shape of the luminous jet is more like that of an ordinary blowpipe flame (b, fig 4)

§ 3 *Experiments with the Various Metals*

The first condition necessary for getting a jet of luminous vapour issuing from the lamp is to have a free evaporation of the cathode metal.   Accordingly it is only with the more volatile metals that the result has been achieved   The list is as follows, roughly in order of volatility—mercury, arsenic, potassium, cadmium, sodium, zinc, magnesium, calcium, antimony, thallium, bismuth, lead, silver, copper

Comparative volatility of the metal is the chief but not the only condition which determines whether the distilled glow will be extensive, and easily maintained

Thus mercury, cadmium, zinc, and magnesium give magnificent effects without difficulty under almost any conditions   Using a plug anode, 2 5 cm long, perforated with a 4 mm. hole, a bright jet 7 or 8 inches high is easily obtained.   With a long channel like this it is necessary to pass rather large currents, causing copious distillation   Thick deposits of finely divided metal may be found on the bell jar, and in the case of magnesium these are sometimes spontaneously inflammable.   It is important to let the bell jar get quite cold before admitting air.

With calcium a very brilliant crimson jet is sometimes seen for a moment, but it has not been found possible so far to get it under control.   A skin apparently forms on the surface of the metal and stops evaporation.   It is probably produced by the action of hot calcium on the quartz tube

a   b

Fig 4

Potassium and sodium give brilliant effects, but are often troublesome, sodium especially   The molten alkali metal froths very badly in the exhausted vessel with evolution of hydrogen, and at times will rise to the anode and well out through the hole   The lamp is then usually short-circuited by an adherent film of metal inside, and has to be dismounted   This trouble makes it necessary to limit the quantity of metal put in. With potassium one of the commercial balls of metal is quite enough, and with sodium rather less is advisable   Another trouble caused by the frothing is that it frequently makes the arc go out   Self-induction in the circuit is specially desirable in these cases   If a long channel is used instead of a diaphragm for the vapour to come out by, it should not be less than 6 mm diameter for these metals

Arsenic and antimony are not deficient in volatility, but the jet of vapour from them does not remain visibly luminous far from the orifice, and the glow is not nearly so striking as in the previous cases   A thin diaphragm must be used with, say, a 3 mm hole

The remaining metals on the list, thallium, bismuth, lead, silver, and copper, are not volatile enough for free distillation unless very hot   In spite of this thallium gave a brilliant and extensive green glow, owing to the great brilliance of the green line, which was the only one visible, or at all events easily visible, in its spectrum   But the other metals have so far given comparatively poor effects   Thin iron anode diaphragms were used so as not to obstruct the issuing vapour, but these are not durable enough to stand very heavy currents, such as would freely evaporate these metals   Anode diaphragms of platinum or tungsten might do better

Something may be said upon the effect of air pressure on the phenomena This is best observed when the lamp has been burning some time so that a steady temperature has been reached, and free ebullition is in progress *   If the metal is one of the more volatile ones, air may be admitted up to a pressure of several millimetres without checking ebullition and causing the luminous jet to disappear   The jet contracts without much change of shape, and becomes intrinsically brighter, but the colour does not usually change. The less volatile metals cannot easily be made hot enough to give a good vapour pressure, thus the jet is only exuded in a high vacuum

An exception to the rule that air pressure does not affect the colour is found in the case of magnesium.   In this instance the jet becomes less blue and more green (increased intensity of the triplet *b*) with increasing air

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* For convenience I include in this term sublimation, at temperatures where the equilibrium vapour pressure of the metal exceeds the air pressure in the bell jar

pressure   The same effect is equally observed when hydrogen is sub-stituted for air, which seems to exclude ʿthe idea that it is due to any chemical interaction of magnesium vapour and air

In the case of many metals there are no marked changes of colour in the jet of glowing vapour as it gets further from the orifice   For instance, in mercury or cadmium such differences are inconspicuous   There are many lines in the spectrum of the glow, and most of these, at all events, decay at the same rate

In other cases there are marked changes   With sodium, for instance, the outer mantle of the jet is yellow, showing little but the D lines (principal series)   Nearer to the orifice, however, the colour is green, and the lines of the two subordinate series (sharp and diffuse) are comparable in intensity with the D lines *   It appears, therefore, that the lines of the subordinate series die out sooner than the D lines

Potassium gives a very bright green inner cone, showing the lines of the two subordinate series   The corresponding lines of the sharp and diffuse series are, as is known, so close together as to give, in a pocket spectroscope, the appearance of a single series, and as no extraneous lines appear, the series relation is probably more striking to the eye in this spectrum than in any bright line spectrum hitherto produced   Nine or ten (complex) lines can easily be seen and photographed   Beyond the end of the series a continuous spectrum is seen   Prof Fowler has pointed out to me that something similar is observed in absorption in the hydrogen stars   Outside the green inner cone shown by potassium vapour there is a faint mantle of a violet colour By analogy with sodium it might be expected that this would show the lines of the principal series   The only representatives of this series in the visual region are in the extreme red and extreme violet and difficult to see   I have not been able to detect them in the spectrum of either the green cone or the violet mantle, though presumably they are there   So far as could be seen, the light of the mantle consists chiefly of the continuous spectrum which has been mentioned as occurring beyond the limit of the subordinate series   It seems, therefore, that this continuous spectrum lasts for a longer time than the series lines

Zinc is another metal which shows a marked difference in duration between different constituents of the spectrum   Near the orifice the spectrum is dominated by the green triplet at 4811.   Further out the light becomes

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* In a preliminary communication to ‘Nature,’ vol. 93, p 32, it was stated that a third and inner zone of all was again yellow, with D lines dominant.   Further observation, under better conditions, has shown that this was an illusion, produced apparently by the greater brightness near the orifice

reddish with the line λ 6363 predominant. The contrast between the inner cone and outer mantle is conspicuous in any case, but becomes more spectacular if the zinc vapour has to force its way out against 1 or 2 mm of air pressure. The luminous jet is then smaller, and the eye does not have to travel so far from the green to the red region Moreover the intrinsic brightness is increased The same device is useful in observing the rather faint violet mantle of the potassium glow already described

Magnesium is a fourth case where colour differences are seen In the inner part of the jet, the predominant colour is green, and is due to the b triplet group The outer part of the jet is dominated by the blue line at λ 4571 characteristic of the flame of burning magnesium In some instances the latter line appears alone in the outer part of the jet, which is then pure blue, but this result has only been obtained occasionally, under conditions not well understood The apparent caprice observed in this case may be connected with the formation of a skin on the cathode surface as with calcium

As already remarked, air pressure in the bell jar makes the outer part of the magnesium glow green, as the core is in any case

In all such cases when one spectrum line outlasts another, the lines of different duration do not belong to the same spectrum series Cases exist, however, where lines belonging to different series appear to have the same duration For instance, the yellow lines of mercury have never been seen to die out either sooner or later than the green line

Earlier investigations by S R Milner[*] and by myself[†] have shown that lines characteristic of the spark do not last so long as arc lines But the observation that different series of arc lines may have different durations is new

In most of the cases above referred to, and in most others, the spectrum of the distilled glow is exclusively a line spectrum The following exceptions have been noted —

Magnesium shows, under favourable conditions, the band spectrum of " magnesium hydride," and this may even rival the line spectrum in aggregate intensity. The hydrogen believed to be necessary for its production is presumably occluded in the metal.

Arsenic gives a glow of slaty grey colour, which consists spectroscopically of broad and regular bands, extending with nearly uniform intensity over the whole visual region

Antimony gives a buff-coloured glow, the spectrum is of the same general

[*] 'Phil. Trans.,' A, vol 209, p 77 (1909).
[†] 'Roy Soc Proc.,' A, vol 88, p. 110 (1913).

character as with arsenic, but the bands are much narrower and more numerous.

Finally, the continuous spectrum beyond the limit of the subordinate series in the alkali metals should be added to complete the list

§ 4 *Summary and Conclusion*

(1) It is known that mercury vapour distilled away from the arc *in vacuo* remains luminous for some distance away from the region of discharge It is now shown how to observe brilliant effects of the same kind from a large number of other metals

(2) As the luminous vapour moves away from the region of discharge, the rate at which different constituents in the spectrum die out is not always the same Thus, for instance, both the subordinate series of lines in the sodium spectrum die out at the same rate, but the principal series dies out more slowly. The lines belonging to any given series always die out at the same rate, but another series may or may not die out at the same rate as the first

(3) In some cases the glowing vapour distilled from the arc shows a band spectrum The alkali metals show a continuous band beyond the limit of the subordinate series like that seen in absorption in the hydrogen stars

The present instalment of this investigation deals only with experimental methods of observing the luminous jets of metallic vapour distilled from the arc and their more obvious features. In the next I hope to discuss the effect of an electric field in quenching the luminosity, and the inferences which can be drawn from the observations generally as to the origin of the radiation and its various spectroscopic constituents.

On a Type-reading Optophone.

By E. E. Fournier d'Albe, D Sc (Lond and Birm.)

(Communicated by Sir Oliver Lodge, F.R.S. Received May 2,—Read
May 28, 1914)

The production of sounds directly or indirectly due to the incidence of
light is the general function of instruments of the type of Graham Bell's
"photophone" An instrument designed to solve the more special problem
of substituting the sense of hearing for the sense of sight is more appro-
priately termed an "optophone."

Having concerned myself for a number of years with this special problem,
I described in 1912 an instrument which enabled sightless persons to locate
bright lights or brightly luminous objects by means of the ear, and to
discover shadows intercepting the light * This result was obtained by
putting two selenium preparations into two arms of a Wheatstone bridge,
sending the galvanometer current through a telephone, and interrupting the
current by a clockwork interrupter A disadvantage of the method was that
the action of the light was not instantaneous

This disadvantage was eliminated in the "reading optophone" described
in 1913 † The audible telephone current was produced by intermittent light
of various musical frequencies, and by using 8 such frequencies, emitted by
dots placed in a row, it was found possible to read transparent letters about
5 cm high by learning to recognise the characteristic sound of each letter
In order to adapt this experimental instrument to the reading of ordinary
letterpress by means of the ear, three further modifications were necessary

(1) The length of the line of luminous dots had to be reduced from 5 cm.
to about 1 5 mm , the size of ordinary type ,

(2) The light had to be used after diffused reflection by the printed surface ,

(3) The sensitiveness of the telephone arrangement had (as a consequence)
to be greatly augmented.

These modifications have now been made, and an instrument has resulted
which should, with some practice, enable totally blind persons to read
ordinary books and newspapers through the sense of hearing

* 'Physikalische Zeitschrift,' vol 13, pp 942–943, Oct 1, 1912 The instrument was
shown at the Optical Convention of the United Kingdom, at South Kensington, on
June 25, 1912.

† 'The Electrician,' vol 72, pp 102–193, Oct 24, 1913. The instrument was shown in
action at Birmingham University, on the occasion of the meeting of the British
Association.

It consists of a small siren disc S, illuminated by a straight Nernst filament N, an optical arrangement for projecting an image of the line of luminous dots furnished by the revolving disc upon the type to be read, a set of selenium or antimonite bridges exposed to the light reflected by the type, a Brown telephone relay connected with these bridges and the telephone receiver used for reading

The optical arrangement consists of a right-angled prism which directs the horizontal beam of light coming from the siren disc upwards through the short-focus portrait lens P on to the small aperture H in the flat slab upon
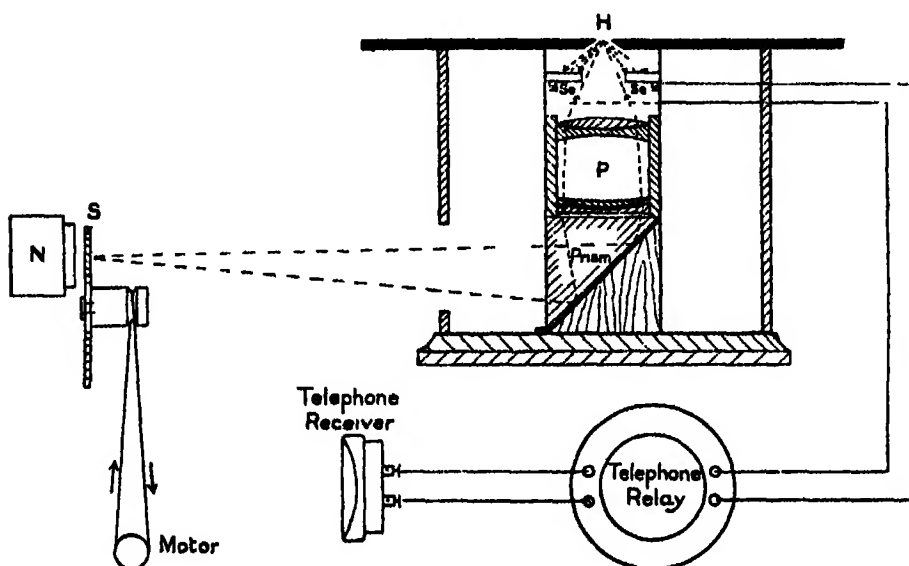
which the sheet of letterpress is laid face downwards   The focal plane of the line of dots coincides with the upper surface of the slab and with the printed sheet

The selenium bridge is placed as closely as possible to the print, and is perforated to allow of the passage of the incident light.

The siren disc is driven by an electric motor or a train of wheels actuated by a weight.   Constancy of speed is desirable, but not absolutely essential

When this is done, and a printed sheet is passed over the slab, the maximum sound is heard in the telephone when the paper exposed is white, and the minimum when it is black   The actual sound heard depends upon the shape of the letter.   The small line of dots, 15 mm long, is made to illuminate each letter in turn, the print being moved steadily in the direction of the printed line, which is at right angles to the luminous line of dots.   The print is so adjusted that the line of dots just covers the

maximum height of the type used   The dots should be at least eight in number, six for the body of the letter, covering the whole height of such letters as *a* and *e*, and one dot each for the upper portion of such letters as *f* and *h*, and for the lower portion of such letters as *p* and *q*

The note of each dot must be chosen so that it is easy to recognise its *omission* (not its *presence*, as in the case of the reading optophone previously described)   Good results have been obtained with a set of notes with which both concords and discords can be obtained, according to the letters exposed Such a series of notes is the following   g c' d' e' g' b' c" e"   But different arrangements may suit different ears

A simple focussing device enables the operator to alter the length of the line of dots, and so adapt it to various sizes of type

It is essential, in reading a line of type, that the alignment be perfect This is ensured by a sliding device on the reading slab

I wish to thank my lecture assistant, Mr A E Vick, for his effective help in constructing the first working model of the instrument, and especially Sir Oliver Lodge for the kind interest he has taken in the whole investigation

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Studies of the Processes Operative in Solutions   XXIX —The Disturbance of the Equilibrium in Solutions by " Strong" and " Weak" Interfering Agents

By H. E ARMSTRONG, F R.S , and E. E WALKER, B Sc

In a recent communication of this series (XXVI),[*] it was contended, that the change in the optical rotatory power of an aqueous solution of fructose which is produced by dissolving in the liquid a second substance, whether this be a salt or a non-electrolyte, is the consequence of an alteration in the proportion in which the two isodynamic forms of the compound are present in equilibrium.   It was shown that substances such as the monhydric alcohols cause the change to take place in a direction opposite to that in which it takes place when substances such as sugar and salts are added: a similar antithesis has been observed in the course of these studies in numerous

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[*] E. E Walker, "The Disturbance of the Equilibrium in Solutions of Fructose by Salts and by Non-electrolytes," 'Roy Soc Proc.,' A, vol 88, p. 246 (1913)

other cases in which the influence exerted by interfering agents has been determined.

To obtain sufficient data for the discussion of this problem, we have not only verified the results previously put forward, by repeating the observations and eliminating unsuspected sources of error, we have also measured the effect of a large number of substances other than those used previously

In making up the solutions, air corrections were applied to all the weighings   The rotatory power of the solution of the fructose used was determined, in each experiment, before adding the interfering agent, as samples of the sugar varied in optical activity over a range of about 0 1 per cent   Two 400 mm polarimeter tubes were used   the lengths of these had been compared by observing the rotations produced when both were filled with the same solution of cane sugar , the readings differed by less than 0 01 per cent.   All measurements were made at 25° C ± 0 005, in mercury green light, with the polarimeter and apparatus described in No XXII of these studies   The rotatory power was determined as soon as possible after adding the interfering agent, as the optical activity tends to increase gradually, especially in presence of the alcohols , usually the reading was taken 30–40 minutes after the temperature of the mixture was constant, in order to allow time for the completion of mutarotation, though in presence of large quantities of alcohol it was necessary to allow a longer interval to elapse, on account of the greatly reduced rate at which the change took place   The rotation produced by the optically active substances which were added was determined at about the same concentration as that at which they were to be used   in calculating the specific rotatory power of the fructose in their presence, the assumption was made that the rotatory power of the added substance was unchanged

The densities were determined by means of density pipettes, the solution being drawn directly into these from the polarimeter tube immediately after the angular deviation had been observed   The quantity of interfering agent referred to is in all cases the amount associated with 100 grm. molecular proportions of hydrone (the fundamental molecule of water) and two molecular proportions of fructose, the volume of such a solution at 25° C being 2030 1 c.c.

Throughout the account, the difference between this volume and the volume of the same solution after the addition of the specified amount of the interfering agent will be represented by ΔV.   The significance of the other symbols that are used is as follows —

M is the molecular proportion of interfering substance present per 100 molecular proportions of water ,

Δ[α] is the change in the specific rotatory power produced by the addition of M gramme-molecular proportions of the interfering substance,

n is the number of atoms of oxygen present in the interfering substance.

Table I *

Interfering agent	No of molecular proportions M	Δ[α]	Δ[α]/M	ΔV/M
Cane sugar	0 633	−1 67	−2 ·64	−212 6
Fructose	1 00	−0 89	−0 89	111 8
Methylglucoside (β)	1 221	−0 68	−0 56	137 2
Dulcitol	0 2485	−0 37	−1 49	120 3
Mannitol	0 765	−0 89	−1 16	120 3
Glycerol	1 373	−0 37	−0 27	71 8
Methanol	3 350	1 50	0 45	37 7
Ethanol	2 360	1 09	0 84	53 ·9
Propanol	1 805	2 13	1 18	69 7
Butanol (normal)	1 496	2 23	1 49	85 4
„ (secondary)	1 481	2 47	1 ·67	85 ·0
„ (tertiary)	1 430	2 21	1 54	86 ·0
, (isoprimary)	1 482	2 24	1 51	85 4
Allylic alcohol	2 ·000	1 64	0 82	63 7
Acetone	1 607	1 71	1 ·06	66 2
Methylethylketone	1 278	1 86	1 45	81 7
Diethylketone	0 603	1 14	1 89	96 4
Methylal	1 897	1 90	0 ·97	79 6
Paraldehyde	0 771	1 15	1 49	122 7
Methylic acetate	1 706	1 ·95	1 14	72 0
Ethylic acetate	1 407	1 49	1 96	88 0
Benzylic alcohol	0 488	0 15	0 31	100 9
Phenol	1 327	−0 51	−0 38	86 5
Cresol	0 2775	−0 01	−0 04	103 0
Quinol	0 930	−1 31	−1 41	89 4
Pyrogallol	0 753	−1 31	−1 71	96 0
Salicin	0 2127	−0 44	−1 88	200 5
Acetonitrile	3 861	3 ·06	0 79	48 1
Propionitrile	2 833	3 39	1 19	64 1
Acetamide	2 615	0 41	0 16	55 8
Urea	2 690	−2 07	−0 ·78	44 9
Methylurea	1 981	−0 28	−0 14	62 ·4
Dimethylurea (symmetrical)	1 920	1 27	0 66	81 5
Diethylurea (unsymmetrical)	1 498	2 21	1 ·47	111 0
Glycine	2 ·000	−3 88	−1 59	45 5
Betaine	1 ·018	0 42	0 42	100 0
Asparagine	0 142	−0 32	−2 2	107 2
Thiourea	1 632	−1 81	−1 11	55 8
Salts —				
Calcium chloride	1 ·054	−3 21	−3 ·04	28 ·3
Magnesium chloride	1 ·054	−2 13	−2 ·02	20 ·4
Ammonium „	2 110	−3 ·26	−1 55	36 ·75
Methylammonium chloride	2 ·000	−2 12	−1 ·06	55 35
Potassium chloride	1 ·556	−3 03	−1 ·95	31 ·0
„ bromide	2 ·000	−4 ·23	−2 ·10	36 ·7
„ iodide	1 ·968	−4 36	−2 22	48 ·2
Monopotassium phosphate	1 ·000	−2 ·73	−2 73	47 ·9
Disodium phosphate	1 000	−1 35	−1 35	6 ·0

* Most of the values in this table are means of two experiments, in which very nearly equal quantities of interfering agent were used

The results are recorded in Table I.* They serve broadly to justify the conclusions previously arrived at As before shown, two classes of effects are produced In the case of the monhydric alcohols and most weak solutes the change in rotatory power is positive presumably such substances promote the formation of fructodextrose, not only sugars, polyhydric alcohols and salts generally (strong solutes) but also phenolic compounds and basic substances such as urea, thiourea and methylurea (though not the higher ureas) and the glycines† have the opposite effect on the rotatory power. they appear to promote the production of fructolævose. It is important to note that, whereas in all cases (except that of the two acetates) the effect becomes more positive as an homologous series is ascended, an accumulation of oxygen atoms involves a change in the opposite direction (compare propanol with glycerol, phenol with quinol and pyrogallol) It is also noteworthy that isomeric compounds usually produce results which differ but slightly (Compare the butanols, dulcitol with mannitol, benzylic alcohol with cresol) Nitrogen appears to have an effect similar to that of oxygen (compare acetonitrile and propionitrile with ethanol and propanol acetamide with urea)

It is not an easy task to interpret the effect produced on fructose in an aqueous solution by various interfering agents, leading as these do presumably to an alteration in the proportions in which the two isodynamic forms are present in equilibrium, the change being sometimes in the one and sometimes in the other direction

Since the previous communication on this subject was published, F P Worley has given an account of a most carefully conducted series of experiments with benzenesulphonic acid‡ (1 molecular proportion to 40 of hydrone) and the three sugars cane-sugar, glucose and fructose (one-quarter of a molecular proportion of each) in which the value of the specific rotatory

* *The Effect of Various Substances on the Rotatory Power of Glucose in Solution.*—The results embodied in the following table, representing the effects produced on glucose, are of the same order as those obtained with fructose, though this sugar is much less sensitive than fructose

Interfering agent		M	1/M Δ[a]
Methanol		6 68	0 14
Ethanol	. . . . .	4·67	0·20
Propanol .	. . .	3·65	0 25
Butanol (tertiary)	. .	2·63	0 32
Glycerol	.	3 65	0 17
Glycine	. .. ..	2·00	−0 15

† It would seem that such substances, though weak solutes, have a specific influence in virtue of their acid or basic character.

‡ These Studies, No. XXI, ' Roy. Soc. Proc.,' A, vol. 87, p. 555 (1912).

power of the sugar alone was determined and also that of the sugar in presence of the acid   The values obtained were —

	Alone	With acid	Difference
Cane-sugar	78 28	77 19	1 ·09
Glucose	62 45	61 29	1 16
Fructose	−104 40	−108 56	4 16

In the case of cane-sugar, in which the possibility of an isodynamic form has not to be considered, as concentration has but little influence on the specific rotatory power, the alteration must be ascribed to the formation of a compound of the sugar with the acid which is of lower rotatory power than the sugar. Cane-sugar is composed of the more dextro-rotatory form of dextrose (the a-form) and of fructodextrose   both "radicles" doubtless combine with acid, though perhaps to a less extent than when they are free   presumably the amount of compound formed from a molecular proportion of cane-sugar would approximate to that formed from a molecular proportion of glucose together with the same quantity of fructodextrose

The effects observed in the case of glucose and fructose—both of which are equilibrated mixtures— are doubtless the algebraic sum of the effects produced on their two isodynamic forms   Judging from Glover's observation that the specific rotatory power of a-methylglucoside is less affected than that of β-methylglucoside by salts, it is probable that the less dextrorotatory form of glucose (the β-form) and fructolævose both combine with acids and salts to a greater extent than the forms of more positive rotatory power   this greater tendency to combine would condition their formation in larger proportion in presence either of an acid or of a salt

The high value deduced by Worley in the case of fructose appears to us to lend support to this view ; from our own observations on the action of salts also we think that the increase in negative rotatory power of fructose is to be attributed mainly to the formation of an increased proportion of fructolævose rather than to the formation of a compound with the acid or salt of specially high negative rotatory power.

Further evidence that the greater affinity of fructolævose to metallic salts is probably the cause which determines the change of equilibrium was obtained from experiments resembling those with alcohol described in No XXVI, p 249   A solution of fructose having been heated to 25°, a weighed quantity of salt was introduced and dissolved as rapidly as possible, the liquid being warmed to compensate for the cooling but never above 25° the solution was then introduced into the polarimeter tube   It was possible

to make the first observation three minutes after adding the salt   A mean value of K was deduced by means of the equation

$$K = \frac{1}{t_2 - t_1} \log \frac{\alpha_\infty - \alpha_1}{\alpha_\infty - \alpha_2}$$

To disturb the equilibrium of the solution, it was then heated to 80° and quickly cooled to 25°   the change in rotatory power was observed as before In the case of the two salts used, the coefficient found was the same whichever way the change was caused to take place, as shown by the results recorded in Table II   It is therefore probable that in the case of fructose the addition of a salt changes the equilibrium between the two isodynamic forms but in a direction opposite to that caused by the addition of alcohol

Table II

Potassium chloride, 1 556 molecular proportions (see Table I)			Potassium bromide, 2 000 molecular proportions (see Table II)		
t	α	K	t	α	K
Mutarotation after displacement of equilibrium by addition of salt					
0	—		0	—	
3	74 41		3	73 90	
6	·89	101	5	74 40	·087
9	75 24	084	7	72	088
12	39	·092	10	75 01	·079
	56		14	23	·087
			19	35	
				41	
	Mean	·092		Mean	·084
Mutarotation after displacement of equilibrium by heat.					
½	72 39	·096	0	68 06	·065
2	73 45	·091	3	71 37	·082
5	74 50	111	6	73 17	·065
8	75 14	·075	9	74 22	·063
14	50		12	79	·078
	70		16	75 17	·062
			21	39	
				53	
	Mean	·095		Mean .	·068

Table III

	KCl	KBr
$a_\infty - a_0$	2 17	2 70
$\dfrac{1}{M} \Delta[\alpha]$ (calculated)	3 2	4 ·0
$\dfrac{1}{M} \Delta[\alpha]$ (observed)	3 03	4 21

If the total change $\alpha_\infty - \alpha_0$ be calculated from the equation

$$\frac{1}{t}\log\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_1} = K,$$

α_0 rotation at time of time of mixing,

α_1 „ „ t, first observation,

α_∞ „ „ end point

The values of $\Delta[\alpha]$ deduced from those of $\alpha_\infty - \alpha_0$ (Table III) approximate sufficiently to the observed values of $\Delta[\alpha]$ to indicate that the change is at least mainly due to the cause specified

From the point of view advocated, the influence of fructose upon itself—that is to say the effect of concentration—is perhaps the most remarkable of all the cases studied the fact that the negative rotatory power increases to a very marked extent as the concentration is increased cannot well be explained except as the consequence of an increase in the proportion of fructolævose In the previous communication, it was contended that fructolævose forms a more stable hydrate than fructodextrose, the implication being that it was the more hydrated compound—if such be the case and it be formed in increasing amount as the solution is concentrated, it must be supposed that the formation of fructolævose is promoted by the tendency it has to combine with itself—to polymerise—much as it is by the presence of a salt with which it can combine

This explanation is that already arrived at in the previous communication and we see no other way at present of explaining our results

It appears logical to explain the action of all substances which increase the negative rotatory power of fructose in this way Salts and cane-sugar and also other substances which have a negative effect doubtless exercise a dehydrating effect: this should promote the formation of fructodextrose, assuming that this form is the less hydrated, but if such be the case, the dehydrating tendency of the interfering agent is masked and overcome by the tendency it has to combine preferentially with fructolævose.

The substances which apparently promote the formation of fructodextrose, as they have a positive effect, do so, it may be supposed, because of the dehydrating effect they exercise—not directly by themselves combining with hydrone but in virtue of their power, as hormones, of dissociating the water

complexes—thus rendering the water more greedy of hydrone (*cf* Part VI)—and also the hydrated fructolævose molecules such substances are to be credited with but slight power of combining either with the fructose molecules or with hydrone and they are far more active mechanically, by their interposition, than are the substances which promote the formation of fructolævose

We may now consider the manner in which interfering agents generally produce the effects we have drawn attention to specially in the case of fructose

Evaluation of the Effects Produced by Interfering Agents

The problem is a very difficult one, on account of its complexity, as the effects considered cannot well be otherwise than the outcome of a variety of adjustments though we are fully conscious that the solution offered can only be regarded as a first approximation, we venture to put it forward for consideration, to provoke further discussion of the issues, as these appear to be of consequence especially in connexion with physiological phenomena *

The one class of interfering agents includes all those neutral, soluble substances which can be classed broadly as *hormones*—substances which diffuse more or less readily through a differential septum such as that with which the barley grain is provided and also promote diffusion of water into the grain the other class includes both the strong electrolytes and substances such as the sugars, in fact *anhormones* generally—*i e* materials which do not diffuse through the differential septum of the barley grain. It would seem to be probable that the special activity of the one class of substances (the hormones) is to be connected with their mobility in solution : that of the other class (the anhormones) with their relative immobility

The difference is not merely that which prevails between electrolytes and non-electrolytes, as sugar and salts produce like effects and as many weak electrolytes are to be ranged with the hormones Apparently, a wider generalisation is possible, inasmuch as the one class includes all substances having a strong affinity with hydrone—the fundamental molecule of water—with which substances of the other class—the hormones—have but slight tendency to associate. As the strong acids and strong bases are among the former, these—the anhormones—may be conveniently spoken of as "*strong solutes*" whilst the other class—the hormones—may be termed *weak solutes.* It is scarcely necessary to point out that the strong shade insensibly into the weak, in fact, that no hard and fast line of demarcation is possible.

It is obviously important to arrive at an understanding of the manner in which the two classes of substance affect the equilibrium in a solution and

* *Cf.* H. E. Armstrong, "The Properties of Alcohol in relation to its Physiological Effects," 'Journ Inst. Brewing,' vol. 19, p. 518 (1913)

to explain the fact that, in some way, they produce opposite effects, this is particularly desirable in view of the special physiological activity of hormones.

Throughout these communications, exception has been taken to the practice of using solutions made up to a particular *volume* (volume-normal solutions) instead of using solutions in which the amount of solvent is maintained constant (weight-normal solutions). In the former case, no constant ratio is maintained between the mass of the solvent and that of the solute, the quantity of the former varying in amount according to the extent to which it is displaced by the solution : in the latter, the only variable introduced consciously is the amount of substance dissolved per unit of solvent and in cases in which the action of an interfering agent is studied, the amount of the interfering agent is alone varied, that of the solvent and solute being kept constant.

In the case of extremely dilute solutions, the two methods yield similar results within the limits of experimental error, as the mass of the solvent is practically proportional to the volume of the solution In the case of concentrated solutions, however, alteration of the amount of solute in a given volume of solution is accompanied by a more or less considerable alteration of the amount of solvent in a given volume, so that there are at least two variables As it is desired to study the effect of the solute on the solvent and *vice versâ*, it is essential that the proportions in which these are present be known therefore weight-normal solutions must be used. When this method is adopted, however, the volume of the solution varies as the proportions by weight of the constituents are altered, so that some part of the change observed may well be due to the variation in the volume distribution of the interacting substances

The question arises whether it be not possible, in some way, to make allowance for alteration in volume and more generally to take into account the purely mechanical, screening action which substances have apart from the influence they exercise through their affinities : this we have endeavoured to answer in the present communication.

Taking into account the effect of alcohols and other substances on—

(1) the rate at which cane sugar is hydrolysed ;
(2) the conductivity of electrolytes ;
(3) the solubility of salts in water ;
(4) the rate at which water enters into the barley grain ,
(5) the rate at which Urea is formed from Ammonic cyanate ,

it will be admitted, probably, that weak solutes (hormones) act mainly in virtue of the dissociating effect which they exercise mechanically within the system into which they are introduced. It might reasonably be expected

that this mechanical effect would be proportional to the change in volume produced by the addition of the interfering agents

In the present communication, an attempt is made to separate the effect of an added substance into two independent components

(1) a purely mechanical, diluent or screening effect which causes *dissociation* of the water complexes, of the complex molecules of the solute and of the hydrates of the solute,

(2) an influence, opposite in effect to the first, proportional to the attractive powers or residual affinities of the admixed substances, promoting *association* in various ways

Table IV

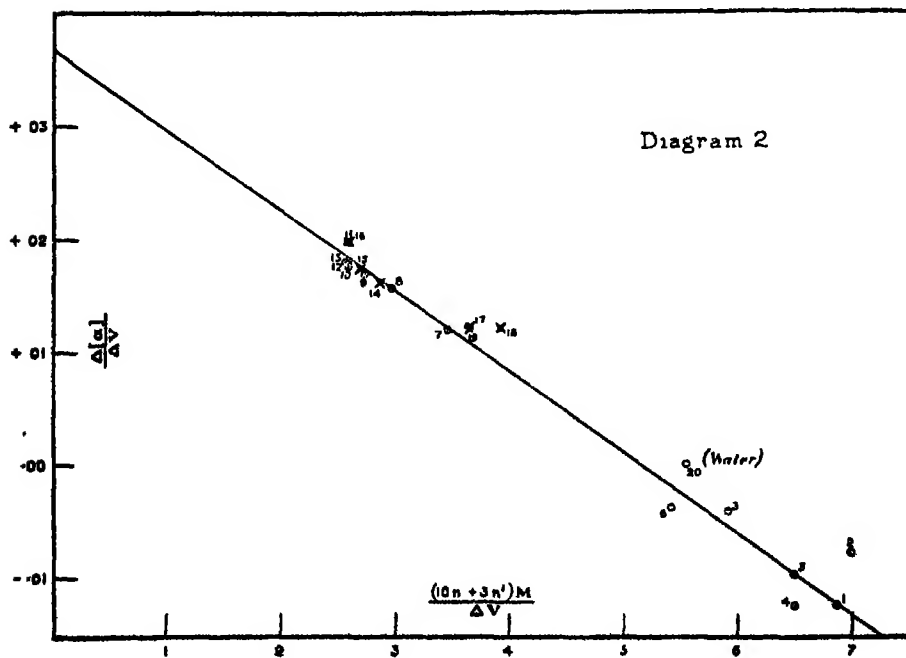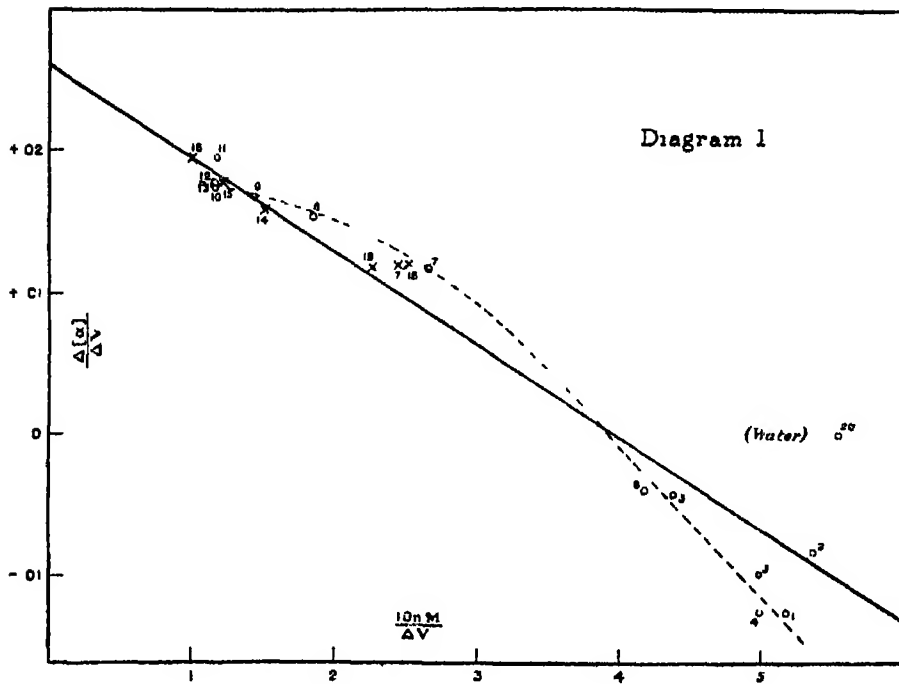| Interfering substance	Diagram 1 $\dfrac{10nM}{\Delta V}$	Diagram 2 $\dfrac{M(10n + 3n')}{\Delta V}$	$\dfrac{\Delta[\alpha]}{\Delta V}$
1 Cane-sugar	0 517	0 686	−0 ·0124
2 Fructose	0 537	0 698	−0 0080
3 Methylglucoside (β)	0 438	0 590	−0 0041
4 Dulcitol	0 499	0 ·648	−0 ·0124
5 Mannitol	0 499	0 649	−0 0097
6 Glycerol	0 418	0 548	−0 0038
7 Methanol	0 266	0 345	0 0119
8 Ethanol	0 186	0 297	0 ·0156
9 Propanol	0 144	0 273	0 0169
10 Butanol (normal)	0 117	0 258	0 ·0175
11 „ (secondary)	0 118	0 259	0 0197
12 „ (tertiary)	0 116	0 256	0 ·0179
13 „ (isoprimary)	0 117	0 258	0 ·0177
14 Acetone	0 151	0 287	0 ·0160
15 Methylethylketone	0 122	0 269	0 0178
16. Diethylketone	0 104	0 259	0 ·0196
17. Methylal	0 252	0 364	0 0122
18 Paraldehyde	0 245	0 392	0 0121
19. Ethylic acetate	0 227	0 364	0 0120
20 Water	0 555	0 555	—

Data for Diagrams 1 and 2

On the assumption that the mechanical effect of the interfering substance is a simple diluent action, proportional to the increase in volume which it occasions, the attempt may be made to evaluate the two effects by comparing the changes in rotatory power caused by the quantities of the interfering agents which produce like changes in volume.

If, within the narrow range covered by the experiments, the change in rotatory power produced by the interfering agent* be proportional to the amount added, the value sought is given by the expression

$$\frac{\Delta[\alpha]}{\Delta V},$$

* When the results quoted in No XXVII (p 393) of these studies are plotted, it is obvious that in the case of alcohol no great error is introduced by this assumption, so

Diagram 1

$\frac{\Delta[\alpha]}{\Delta V}$

$\frac{10n\,M}{\Delta V}$

(Water)

Diagram 2

$\frac{\Delta[\alpha]}{\Delta V}$

$\frac{(10n+3n')M}{\Delta V}$

(Water)

the change of rotatory power produced by the quantity of substance which causes an increase in volume of 1 c c in a solution of 2 gramme-molecular proportions of fructose in 100 of hydrone

In Diagram 1 this quantity is plotted against the number of grammes of oxygen in the quantity of interfering agent used $nM/\Delta V$ (see Table IV) Though the various points are not strictly in line, nevertheless, a very general relationship between the effect produced by a paraffinoid oxygen compound and the number of oxygen atoms it contains is obvious. A straight line drawn between the points cuts the rotation axis at about $+0\ 026$, this value may be taken as a first approximate expression of the effect which would be produced by 1 c c (apparent) of a substance free from oxygen

A closer study of the diagram reveals the fact that all substances (*i e* paraffinoid alcohols and sugars) lie on a curve (the dotted line) rather than on a straight line   This may mean · either that the activity of the oxygen varies as the amount present is increased—or that the hydrocarbon radicle itself has a chemical activity which cannot be neglected—or still more probably that both of these causes are at work. It is, however, interesting to note that the curvature can be eliminated if the assumption be made that the methylene group has an influence just about one-third as great as that of the oxygen atom

If the ordinates are calculated from the expression

$$\frac{M(10n+3n')}{\Delta V},$$

in which n' is the number of carbon atoms in the molecule, Diagram 2 is obtained. The points in this diagram lie very near to a straight line and the value of the hypothetical substance having no residual affinity is raised to $0\ 037$. It is to be noticed that water, which may be regarded as the lowest alcohol, now comes into line with the polyhydric alcohols, this is an important argument in favour of the view that carbon is in part responsible for the effect produced, as it is only when this is taken into account that water is brought into line with the compounds containing carbon

Using the value $0·026$ arrived at in Diagram 1 as the "volume-coefficient," the change in rotatory powers per gramme molecular proportion of substance added, viz $\Delta[\alpha]/M$ is equal to $0\ 026\ \Delta V/M - A$, in which A is the residual affinity or chemical effect per gramme molecular proportion: whence it follows that

$$A = 0\ 026\Delta V/M - \Delta[\alpha]/M.$$

long as the change in rotatory power does not exceed 3° or 4°, a quantity not exceeded in the observations we are discussing (*cf.* Wenden, 'Biochem. Zeit.,' vol 30, p. 357).

By substituting 0 037, the value of the volume-coefficient arrived at in Diagram 2, other values of A are obtained. but since these are obtained on the assumption that carbon has a value equal to about one-third that of an oxygen atom, this value must first be subtracted before the variation of A can be correlated with the number of oxygen atoms in the molecule

$$A = A' + 0\ 23n' = \frac{1}{M}(0\ 037\Delta V - \Delta[\alpha])$$

The coefficient 0 23 is chosen by trial, approximately one-third the mean value of A'/n

Influence of Oxygen Compounds

In Table V are given the values of A found in the case of a series of paraffinoid oxygen compounds It will be noticed that these values differ considerably in the case of different compounds on dividing them, however, by the number of oxygen atoms in the molecule, approximately constant values (column 5) are obtained in other words, the chemical effect is approximately proportional to the number of atoms of oxygen in the molecule Though only another way of expressing the result arrived at by means of Diagram 1, this has the advantage that it is applicable to substances containing radicles other than oxygen The two compounds in which the departure is greatest are allylic alcohol and methylic acetate, the value in

Table V

Interfering substance	$\dfrac{0\ 026\,\Delta V}{M}$	$\dfrac{\Delta[\alpha]}{M}$	A	$\dfrac{1}{n}A$	$\dfrac{1}{n}A'$
Cane-sugar	5 53	−2 64	8 17	0 74	0 71
β Methylglucoside	3 57	−0 56	4 13	0 69	0 67
Fructose	2 81	−0 89	3 70	0 62	0 61
Dulcitol	3 13	−1 49	4 62	0 77	0 76
Mannitol	3 13	−1 16	4 29	0 72	0 70
Glycerol	1 87	−0 27	2 14	0 71	0 74
Methanol	0 08	0 49	0 53	0 53	0 72
Ethanol	1 40	0 84	0 56	0 56	0 ·70
Propanol	1 81	1 18	0 63	0 63	0 ·71
Butanol (normal)	2 ·22	1 49	0 73	0 73	0 75
„ (secondary)	2 21	1 ·67	0 54	0 54	0 ·56
„ (tertiary)	2 24	1 54	0 70	0 70	0 74
„ (isoprimary)	2 ·22	1 51	0 71	0 71	0 73
Allylic alcohol	1 ·66	0 82	0 84	(0 84)	(0 85)
Acetone	1 72	1 ·06	0 ·66	0 66	0 ·70
Methylethylketone	2 12	1 45	0 67	0 ·67	0 65
Diethylketone	2 51	1 89	0 62	0 ·62	0 53
Methylal	2 07	0 ·97	1 10	0 55	0 64
Paraldehyde	3 19	1 49	1 70	0 57	0 53
Methylic acetate	1 87	1 14	0 ·73	0 37	0 42
Ethylic acetate	2 29	1 06	1 ·23	0 ·61	0 ·64
Water	0 47	—	0 47	(0 47)	0 66

the former case being high and in the latter low that of the acetate is the more remarkable departure, as the ethylic salt affords a "normal" value. The high value given by allylic alcohol is undoubtedly to be connected with its ethenoid structure

The values obtained on using the more complex hypothesis, viz, that the carbon has an effect equal to about one-third that of the oxygen atom, are given in Column 6, A' being the value arrived at by making allowance for the number of carbon atoms present The values deduced for alcohols, on this hypothesis, are more nearly alike, most of them lying between about 0 70 and 0 75

Table VI contains the values of A deduced in the case of several benzoid compounds The apparent influence of the benzene radicle is evaluated by subtracting $0 65 n$, the mean value of an oxygen atom (Table V) for each oxygen atom present in the molecule It is obvious that the phenyl group has a very special influence, either directly or indirectly

Table VI —Values of A for Benzenoid Compounds showing the Influence of the Benzene Complex

Interfering agent	$\dfrac{0\ 028\Delta V}{M}$	$\dfrac{\Delta[\alpha]}{\Delta V}$	A	n	$A - 0\ 65n$
Benzylic alcohol	2 62	0 31	2 31	1	1 7
Phenol	2 ·25	−0 88	2 63	1	2 0
Cresol	2 68	−0 04	2 72	1	2 1
Quinol	2 ·32	−1 41	3 73	2	2 4
Pyrogallol	2 50	−1 74	4 ·24	3	2 3
Salicin	5 24	−2 06	7 30	7	2 8*

* If 0 69, the mean value of A/n in sugars and hexahydric alcohols, be used, the value for the benzene radicle in column 5 is reduced to 2 2 and so made more nearly compatible with the others

In dealing with the nitrogen compounds and certain benzene derivatives the second hypothesis will not be taken into account

Influence of Nitrogen Compounds.

The values of A deduced for a series of nitrogen compounds (Table VII) are of interest as showing that, as observed in the case of other properties, the effect* of this element is far less " constant " than that of oxygen The effect of the nitrogen in the two nitriles is about the same , urea has about the same

* The apparent effect of the nitrogen atom is obtained by subtracting 0·65n from A and dividing by n'', the number of nitrogen atoms in the molecule See last column, Table VIII

value as acetamide, which presumably contains nitrogen in the same form of combination. The values of the substituted ureas, on the other hand, are lower, methylurea being lower than urea and dimethylurea still lower In glycine, betaine and asparagine, either nitrogen or oxygen must have abnormally high values· it is noteworthy that, just as the value of A in urea is reduced by the substitution of the amido hydrogen by methyl, so is the corresponding value of glycine reduced by the substitution of the atoms of hydrogen attached to nitrogen, it is reduced by a little more than the difference between urea and unsymmetrical diethylurea Obviously these differences invite further enquiry

Table VII

Interfering substance	$\dfrac{0\ 026\Delta V}{M}$	$\dfrac{\Delta[a]}{M}$	A	Value of oxygen (assumed)	n''	$\dfrac{A-0\cdot 65a}{n''}$
Acetonitrile	1 25	0 79	0 46		1	0 46 ⎫
Propionitrile	1 66	1 19	0 ·47		1	0 47 ⎬
Acetamide	1 45	0 16	1 29	0 65	1	0 64 ⎫
Urea	1 17	−0 78	1 95	0 65	2	0 65 ⎬
Methylurea	1 62	−0 14	1 76	0 65	2	
Dimethylurea (symmetric)	2 12	0 66	1 46	0 65	2	0 41
Diethylurea (asymmetric)	2 89	1 47	1 42	0 65	2	
Glycine	1 18	−1 50	2 77	1 3	1	1 47
Betaine	2 60	0 42	2 18	1 3	1	0 88
Asparagine	2 79	−2 2	5 0	1 ·05	2	1 5
Thiourea	1 45	−1 11	2 50		2	

Influence of Salts

The results obtained with a number of haloids and with the two phosphates are given in Table VIII The marked difference between the values of A in

Table VIII —Values of A calculated for various Inorganic Salts

Interfering agent	·026ΔV/M	$\dfrac{\Delta[a]}{M}$	A
Magnesium chloride	0 ·53	−2 02	2 55
Calcium chloride	0 74	−3 04	3 78
Ammonium chloride	0 96	−1 55	2 51
Methylammonium chloride	1 44	−1 06	2 50
Potassium chloride ..	0 81	−1 ·95	2 76
„ bromide	0 ·95	−2 10	3 ·05
„ iodide	1 25	−2 22	3 47
Disodium phosphate	0 ·16	−1 35	1 51
Monopotassium phosphate	1 ·24	−2 ·73	3 97

the case of the three potassium salts is in accordance with the view generally held that the residual affinity of salts depends chiefly on the acid radicle, though this is influenced by the metal, as shown by the difference between magnesium and calcium chlorides   The considerable differences between ammonium and methylammonium chloride in the values of $\Delta[\alpha]/M$ and the close similarity of the values of A are indications that the difference is chiefly due to the volume effect of the methyl group

Precipitation of Salts.

It now remains to be seen how far the conception of the existence of two opposing forces can be used to explain other effects of dissolved substances on solutions

Table IX—Values of A and A/n calculated from the Effect of various Substances on the Solubility of Potassium Chloride in Water

Interfering agent	M	$10 \log_e \frac{S_2}{S_1}$	ΔV	10 A	n	10A/n
Glucose	1·00	0 365	121 1	3 99	6	0 66
Mannitol	0 215	0 008	26 8	3 79	6	0·63
Glycerol	0 25	−0 027	17 6	1 94	3	0 65
Glycol	1 00	−0 237	51 1	1 29	2	0 65
Methanol	3 00	−1 164	93·9	0 55	1	0 55
Ethanol	2·00	−1 309	88 6	0·67	1	0 67
Propanol	1·00	−0 965	54 5	0 67	1	0·67
Paraldehyde	0·0833	−0 127	8 7	1 6	3	0 58

S_1 = solubility of potassium chloride.
S_2 = solubility of potassium chloride in presence of interfering agent

The equilibrium between a solid salt and its aqueous solution may appear to be very different from that of two isodynamic forms of fructose · nevertheless there are points of similarity in the problem. The equilibrium in a saturated solution may be represented thus:—

$$\text{Salt } (H_2O)_x \rightleftharpoons \text{Salt} + xH_2O,$$

a process which has something in common with the conversion of fructose into a less hydrated form   The case is complicated, however, by the fact that the quantity of salt in solution varies at the same time as that of the added substance   The extent of the influence due to this variation is not known: the assumption may be made, however, that its magnitude is proportional to the change in concentration so long as this is small. We may therefore write—

$$A = \frac{1}{M}(C\Delta V + \Delta S + C'\Delta S),$$

in which ΔS is the increase or decrease in solubility, C' a constant depending on the magnitude and sign of the influence referred to above.

It is obvious that the quantity C' affects C and A to the same extent and will not interfere with the relationship between them—

$$\frac{A}{1+C'} = \frac{1}{M}\left(\frac{C}{1+C'}\Delta V + \Delta S\right) \quad \text{or} \quad A'' = \frac{1}{M}(C''\Delta V + \Delta S),$$

and therefore need not be expected to have a very great influence

ΔS can only be used for very small percentage changes in solubility Rothmund has shown[*] that the influence of a substance on solubility is approximately proportional to the logarithmic function, $\log \frac{S_2}{S_1}$, this has been used in calculating the values of A given in Table IX from data supplied by Armstrong and Eyre[†] The value 0 030 deduced graphically has been assigned to C and values of A calculated according to the equation ·

$$A = \frac{1}{M}\left(0\ 0031\Delta V + \log_e \frac{S_2}{S_1}\right)$$

The values show that a general relationship exists between the values of A and the number of oxygen atoms in the molecule

The Hydrolysis of Cane-sugar

Whilst neutral salts increase the rate at which cane-sugar is hydrolysed, alcohols, as Caldwell and Worley have shown, have the opposite effect In such a case, as changes may take place in the catalyst as well as in the substance which is changing, the velocity at which a chemical change takes place is subject to the action of a number of factors in excess of those by which a change in the equilibrium of two isodynamic substances is influenced nevertheless, it is clear from Caldwell's values that the influence exercised by lactose, glucose, glycerol and ethylic alcohol is of the same order as that which these substances exercise on the solubility of salts and on the equilibrium of the two forms of fructose.

The chief difficulty that arises in attempting to evaluate their influence is to decide on a method of expressing the increase or decrease in the rate of hydrolysis when this is a large percentage of the whole change. in default of further knowledge, the following expression has been used .—

$$A = \frac{1}{M}\left(0\ 0021\Delta V - \frac{K_2 - K_1}{K_2}\right)$$

$K_1 =$ Velocity coefficient in absence of interfering agent,
$K_2 =$ „   „   in presence of   „

[*] 'Zeit. Phys. Chem ,' vol 69, p 523
[†] 'Proc. Roy Soc.,' A, vol 79, p 566 , vol. 84, p 123

This has been applied to the data given by Caldwell   The results, though few in number, tend to show that the two opposing forces contemplated are at work governing the rate at which the chemical action takes place   Values of A, giving C the value 0 021, are shown in Table X

Table X —Values of A of various Substances calculated from their Effect upon the Rate at which Cane-sugar is Hydrolysed by Chlorhydric Acid

Interfering agent	M	ΔV	$0\cdot021\,\Delta V$	$10\,\dfrac{K_2-K_1}{K_2}$	10A	n	10A/n
Lactose	½	110 6	2 32	0 09	4 64	11	42
Glucose	1	120 2	2 53	0 16	2 68	6	45
„	½	57 1	1 20	0 09	2 58	6	43
Glycerol	1	75 8	—1 59	—0 49	1 10	8	37
Alcohol	1	59 8	1 26	—0 84	0 42	1	42
(NH$_4$)Cl	1	44 4	0 93	3 06	3 99		
KCl	1	31 6	0 66	3 27	3 93		
NaCl	1	18 8	0 39	4 47	4 86		
BaCl$_2$	1	33 6	0 70	9 28	9 98		

Velocity of Chemical Action in Various Solvents.—Patterson and Montgomerie[*] have collected a number of cases in which the velocity of chemical action has been compared in different solvents   On account of the regularity of the order in which solvents are active in various cases, it is at least probable that their residual affinity plays an important part.

Values of AM/ΔV, reduced to that of methylic alcohol as unity, are given in the first column of Table XI

Table XI

Solvent	A $\dfrac{M}{\Delta V}$	Menchutkin	Patterson and Montgomerie
Methanol	1 ·00	1 00	1 00
Ethanol	0 74	0 71	0 90
Propanol	0 64	—	0 82
Butanol	0 59	0 ·50	0 46
Allylic alcohol	0 95	0 84	0 75
Benzylic alcohol	1 ·64	2 59	1 52

This quantity is practically the " amount " of residual affinity per cubic centimetre   The values in columns 2 and 3 are the velocity coefficients reduced to that of methylic alcohol, in the case (A) of the interaction of triethylamine and ethyl iodide (Menchutkin) ; (B) of the transformation of syn-anisaldoxime into anti-anisaldoxime (Patterson and Montgomerie).

* ' Trans. Chem Soc,' vol. 101, p 34 (1912)

The similarity between Menchutkin's values and those in the first column is striking   Patterson and Montgomerie's values are not so closely in agreement with those calculated, though the order, excepting in the case of allylic alcohol, comes out the same

Taking into account the results arrived at by applying our method to a variety of interactions very different in character, in view of the broad agreement with the hypothesis considered, we venture to think that it has been justified and that the discussion will serve to overcome the reluctance with which weight-normal solutions are used

Senter, in a recent reference to certain communications of this series of studies, criticises the use of such solutions   while admitting that the method has considerable advantages, he states that it has one serious disadvantage *from the point of view of the kinetic theory*   Taking the case of the hydrolysis of cane-sugar as an example, he asserts that the mean free path of the interacting molecules depends on the total volume and that, other things being equal, the velocity of interaction must depend therefore on the total volume

We have difficulty in understanding this argument and its application to our work   If it be desired to study the effect of a third substance C on the interaction of A and B in solution in some liquid, without varying the proportions of A and B to the solvent, so that there may be only one variable, no other method is possible than that of merely adding the desired amount of C   C then exercises a certain screening effect and would equally exercise the effect whether the solution were made up to a definite volume or by weight   Our desire in this communication has been to contrast the effect produced by the substance as a mere screen with that which it exercises in other ways, so that we might be in a position to form an estimate of the " chemical " effects produced by various substances.

The results obtained by means of the method appear to justify the conclusion that in the case of the homologous alcohols, for example, when allowance is made for the screening effect they exercise, their molecular chemical activity varies but slightly throughout the series, moreover, that the activity per atom of oxygen in related paraffinoid compounds is practically the same.   It seems to us, therefore, that we have devised a method of treatment by means of which many diverse phenomena manifest in solutions may be correlated

Similarity of Motion in Relation to the Surface Friction of Fluids.

By T. E. Stanton and J. R. Pannell

(Abstract.)

The paper deals with an experimental investigation of the similarity of motion in fluids, of widely different viscosities and densities, in motion relative to geometrically similar surfaces, the existence of which has been predicted from considerations of dynamical similarity by Stokes,[*] Helmholtz,[†] Osborne Reynolds,[‡] and Lord Rayleigh.[§]

The theory in its most general form may be expressed by the relation given by Lord Rayleigh

$$R = \rho v^2 f\left(\frac{v L}{\nu}\right),$$

where R is the resistance per unit area of the surface, ρ the density of the fluid, v the velocity, L a linear dimension of the surface, ν the kinematical coefficient of viscosity of the fluid, and the assumptions made in the derivation of the expression are that R depends solely on ρ, L, v, and ν.

The method of experimentally demonstrating the sufficiency of these assumptions has been by a determination of the surface friction of air and water flowing through smooth pipes of varying diameters and with as great ranges in velocity as possible, and so obtaining values of the conditions for similarity of motion, which is that for the same values of vd/ν in either fluid the values of $R/\rho v^2$ should be identical.

The experiments show that this condition is fulfilled in the case of commercially smooth brass pipes with considerable accuracy through a range in the value of vd/ν of from 2500 to 430,000. To obtain this range with the comparatively small diameters of pipes used, mean velocities of flow up to 6000 cm. per second have been reached.

From these data it has been possible to investigate the limits of accuracy of the well-known index law of the resistance of fluids, $R = kv^n$, which

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[*] 'Mathematical and Physical Papers,' vol. 3, p. 17.

[†] 'Wissenschaftliche Abhandlungen,' vol. 1, p. 158.

[‡] 'Phil. Trans.,' 1883, p. 935.

[§] 'Phil. Mag.,' 1899, vol. 48, p. 321, 'Report of Advisory Committee for Aeronautics, 1909—1910, p. 38.

was found by Osborne Reynolds to express the resistance with fair accuracy from $vd/\nu = 2500$ (at the critical velocity) to $vd/\nu = 80,000$ The authors' experiments confirm this conclusion, but show that, when the range is extended to $vd/\nu = 430,000$, the index law fails when applied to the whole range

The paper also contains an experimental determination of the variation of the ratio of the mean velocity to the maximum velocity of fluids in pipes through a range in vd/ν from 2500 to 72,000, and shows that the ratio is not constant, as has been supposed, but is a function of vd/ν

The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility.

By A E Oxley, B A , M Sc , Coutts Trotter Student, Trinity College, Cambridge

(Abstract)

On the hypothesis that the molecules of liquid and crystalline substances are distorted by the forces exerted on them by the surrounding molecules, it may be expected that the transition from the liquid to the crystalline state will be accompanied by a change in the specific magnetic property of the substances to an extent dependent upon the nature of an individual mole-cule and its grouping with other molecules * If this change of specific diamagnetic susceptibility be noted by $\partial\chi$, we may write

$$\partial\chi = \chi_c - \chi_l = \frac{N}{H}(\Delta M_c - \Delta M_l),$$

where χ_c and χ_l are the specific susceptibilities of the crystals and the liquid, and ΔM_c and ΔM_l are the diamagnetic moments induced in a distorted molecule of the crystalline and liquid states, respectively, by the application of a magnetic field H N is the number of molecules per gramme of the substance.

In the present investigations, about 20 organic substances, most of which are of an aromatic nature, have been examined and the results are recorded in Part I of the main communication.

A large number of experiments have been made on the variation of the specific susceptibility (χ) over an interval of temperature ranging from

* See 'Camb. Phil Soc. Proc.,' vol 16, p. 466 (1912)

$-150°$ C to $200°$ C. For details concerning the method of experiment and the elimination of errors due to disturbing sources reference is made to the main paper

It has been found that the Curie law of constancy of diamagnetism holds for most of the substances, to within the limits of experimental error, providing there is no appreciable change of molecular constitution with variation of temperature. During the transition from the liquid to the crystalline state there is an appreciable change of χ, which amounts with benzene derivatives to 5 per cent (approximate) of the susceptibility Nitrobenzene is exceptional and gives an abnormally large value of $\partial\chi/\chi$ If the substance does not crystallise but passes into a super-cooled liquid or jelly state, the value of $\partial\chi$ is too small to be detected   This jelly state was obtained with many of the compounds examined

This result is in accordance with the observations of M Chaudier,* who has investigated, for these same substances, the variation of the magnetic rotatory power which accompanies the passage from the liquid to the crystalline state   According to Chaudier the magnetic rotation of the super-cooled liquid or jelly is the same as that of the liquid above the normal fusion point, but if the substance crystallises the rotatory power disappears completely

With benzophenone a complete hysteresis loop with respect to temperature has been obtained, similar to those discovered by the late Prof Hopkinson in the case of nickel-steels   The fusion point of the diamagnetic crystals corresponds to the critical temperature of the nickel-steel and the heat of formation of the crystals in the former case to the heat evolved (recalescence) at the critical temperature of the nickel-steel.

The general results are considered in connection with our knowledge of crystal structure, with which they are consistent if the appearance of the crystalline state implies a small deformation of the molecules

It appears that the diamagnetic property of substances is complex and very similar to the magnetic property possessed by ferro-magnetic substances above and below the critical temperature   The only difference between the two types of phenomena is due to the nature of the magnetic moment associated with an individual molecule and by the variation of which the changes of molecular constitution are disclosed

In Part II a theoretical interpretation of the effects which have been observed is given   The electron theory of magnetism developed by M. Langevin† for the gaseous state is extended by taking into account the mutual forces between the molecules of the liquid and crystalline states. These forces

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* 'Compt Rend,' vol. 156, p. 1529 (1913).

† 'Ann de Chim. et de Phys,' sér. viii, vol. 5, p. 70 (1905).

produce a polarisation effect in every molecule, and if a_c and a_l are the polarisation constants of the crystalline and liquid states respectively, then, interpreting the distorting forces magnetically, it has been shown that

$$\frac{\partial \chi}{\chi} = (a_c - a_l) \ \frac{\Delta H}{H},$$

where a_l ΔH is a small adjustment of the applied magnetic field, H, due to the alteration of the self-induction of the electron orbits which accompanies an exceedingly small deformation of the molecules of a substance in the liquid state, and a_c ΔH is the corresponding adjustment associated with the crystalline state

a_l is of the order $1/3$ and is negligible in comparison with a_c, which is at least of the order 100 and probably is much greater   This minimum value of a_c was deduced from Chaudier's observation that the magnetic rotatory power of aniline, benzene, and nitro-benzene disappears completely on crystallisation   The relatively small value of a_l for the liquid state is due to an average polarisation effect produced by the random distribution of orientations of the surrounding molecules, whereas the value of a_c for the crystalline state depends upon the fact that the surrounding molecules are definitely orientated with respect to any particular molecule

The large value of a_c leads at once to the representation of the change of χ when the substance crystallises as due to a *mean* molecular field in the diamagnetic medium, which takes the place of the effects produced by the mutual forces between the molecules, and which may be written in either of the forms

$$a_c \cdot \Delta H, \quad \text{or} \quad a_c' \ N \ \Delta M \ \rho,$$

where N ΔM ρ is the intensity of magnetisation of the substance, ΔM being the diamagnetic moment induced in the molecule and ρ the density of the substance   This is analogous to the interpretation, given by M Weiss, of the mutual influences of the molecules of a ferro-magnetic substance by means of a molecular field **NI**, where **I** is the saturation intensity of magnetisation of the ferro-magnetic substance and **N** is the constant of the ferro-magnetic field   The order of magnitude of a_c' and **N** is the same, and this leads to the conclusion that the *local* molecular field in diamagnetic substances (at least those substances which have been examined) is comparable with the molecular field in ferro-magnetic substances   Such a large local molecular field would account for the rigidity of crystal structure in general

Several extensions of this work have been completed and the conclusions which have been obtained are in harmony with those already described.   I hope to publish an account of these extensions soon

# On the Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles

By W I Pawlow

The object of the present research was to investigate the ionising properties of positive ions using a direct method, and to try experimentally to determine the minimum energy which is necessary for a positive ion to produce fresh ions by collision with a gas molecule   At the same time it appeared to be of interest to measure the ionising potential for negative corpuscles under experimental conditions somewhat different from those previously adopted

§ 1 Description of the Apparatus

The apparatus in the present investigation was used in two forms, represented in figs 1 and 2   The part common to both forms consists of two

Fig 1

Fig 2
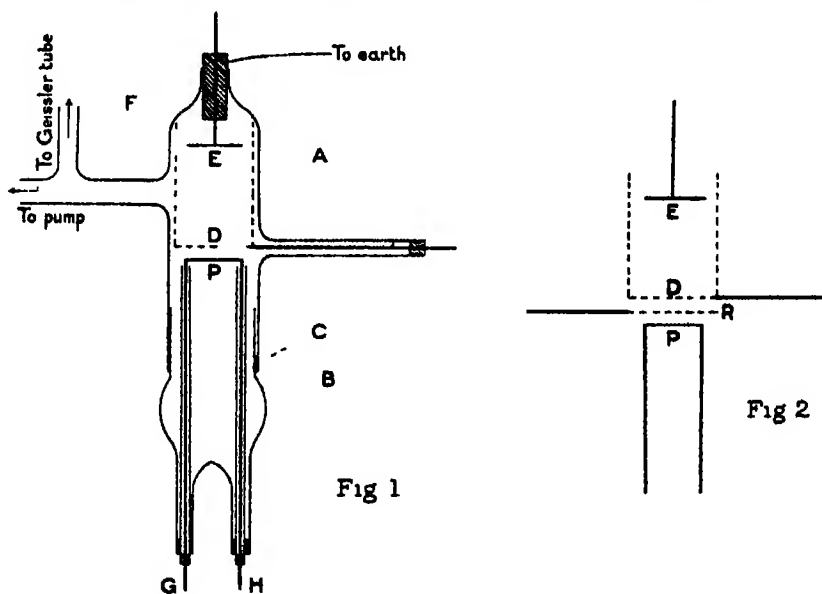
pieces of glass tubing, A and B—A, 3 5 cm in diameter, B, a little less—the latter being blown out to a slightly spherical form, as shown in the diagram   The joint at C was made air-tight with sealing wax. By this means it was possible to take out the lower part very easily—a process which was very often necessary in order to renew the platinum strip P,

or to cover it with a fresh salt   In the narrow upper part of the tube A a brass rod was sealed with a round brass plate E at its end.   This rod was insulated and surrounded by a brass tube connected to earth, to prevent it acquiring a charge from the glass   The plate E was used as an electrode to measure the ionisation, and was connected to a Wilson's tilted electroscope adjusted to a sensitiveness of 80 divisions per volt   The ionisation chamber was a wire-gauze cylinder D, through the open top of which passed the electrode E.   The sides of the cylinder were made of brass gauze and the bottom of platinum gauze, which was fixed in clamps at the end of a brass rod which passed through a side tube and which held the cylinder in its proper position   The platinum strip P was of thin foil, 2 cm long and 1 mm wide   It could be heated electrically by means of the thick copper leads G and H, the current being supplied from a battery of six accumulator cells connected in parallel and regulated by wire resistances   The heating circuit was insulated   The copper leads G and H were covered with glass in order to make them more rigid and to keep them cool   These glass tubes and the leads themselves were sealed into two tubes joined to the spherical part of the lower tube.   The tube B could be adjusted at the joint C, so as to fix the strip P at any distance from the bottom of the cylinder D

The second form of apparatus differs only in having in the upper tube an additional side tube through which passes a brass rod holding a platinum gauze R, as shown diagrammatically in fig 2   The gauze is parallel to the bottom of the cylinder, and is placed between the latter and the platinum strip P   The distance between the plate E and the gauze D in the different experiments was changed from 4 to 5 cm   The distances from D to R, and from R to P, varied from 1 to 2 5 mm in different experiments   The wide tube connecting the apparatus to the gauge, pump, phosphorus pentoxide drying tube, and charcoal tube, was sealed into the upper part of the apparatus opposite the ionisation chamber   The platinum strip itself served as a source of negative corpuscles   In the experiments with positive ions the strip was covered with a layer of sodium phosphate, which was formed as usual by evaporating a water solution of the salt by gradually heating the strip.   Sodium phosphate was chosen as a very intense[*] source of positive ions   In some of the first experiments aluminium phosphate was used

§ 2 *Experimental Results.*

The method used in these experiments is originally due to Lenard[†] and was applied by him to the determination of the ionising potential for negative

[*] F Horton, 'Roy Soc. Proc,' A, vol 88, p 138 (1913)
[†] P Lenard, 'Ann der Phys ' (4), vol 8, p. 188 (1902).

corpuscles   This method was subsequently used by v Baeyer,* Dember,†
and Franck and Hertz‡ for the same purpose.

The experimental arrangements in the first form of apparatus were similar to
those used by Franck and Hertz (*loc cit*), in their investigation of the ionising
potential for the negative corpuscles, but in the present case, for the investiga-
tion of the positive ions, the potentials were of opposite sign   The platinum strip
P was permanently charged to a negative potential V_1 volts, and the negative
potential V_2 volts of the cylinder D was gradually altered, being always greater
in its numerical value than V_1 The plate E was initially connected to earth,
thus the electric force between the strip and the bottom of the cylinder was
directed upwards, while the force inside the ionisation chamber was in the
opposite direction   During the observations the earth connection of the
plate E was broken, and the electric charge obtained by the plate was
measured on the electroscope   In these conditions the positive ions emitted
by the heated salt first went through the accelerating field of $(V_2 - V_1)$ volts,
and entering the ionisation chamber were subjected to a still stronger
retarding field of V_2 volts which prevented them from reaching the upper
electrode E   The distance between P and D over which the accelerating field
was applied was much smaller than the mean free path of the positive
particles at the pressures used in the experiments.   The distance between D
and E over which the retarding field was applied was, on the contrary, much
larger than the mean free path   One of the necessary conditions of the
experiment is to communicate the energy to the positive ions during their
free path.   If the only source of the ionisation were the heated salt, emitting
positive ions, the electroscope ought not to show any charge   If, however, the
positive ions, after entering the ionisation chamber but before being stopped
by the retarding field, came into collision with the molecules of the gas and
ionised them, the negative corpuscles thus produced would be carried by the
field V_2 to the electrode E and would thus communicate a negative charge to
the electroscope   As a matter of fact, the electroscope showed a strong
negative charge, confirming the presence of carriers of negative electricity in
the gas under the action of the positive ions   By altering the value of the
potential V_2 it was possible to investigate the change of the negative charge
with the energy of the positive ions by which it was produced.   In all
subsequent values of the velocity of the charged particles, the fall of potential
in the heated strip itself was taken into account   One end of it had a
potential from 1 to 2 volts higher than the other end and in all results the

* O v Baeyer, ‘ Deutsch. Phys. Ges Verh ,’ vol 10, p. 96 (1908)

† H. Dember, ‘ Ann der Phys.’ (4), vol 30, p. 137 (1909).

‡ J. Franck and G Hertz, ‘ Deutsch. Phys. Ges Verh.,’ vol. 15, p. 34 (1913)

velocity given corresponds to the higher value of the accelerating field   As an illustration of the type of curves obtained, the values for H_2, O_2, N_2 observed at the pressure 0 008 mm are plotted in fig 3   The actual numbers were reduced to the same scale so as to start from the same value of the ionisation at the point corresponding to the largest velocity used   The curves are all of similar form and approach the axis of x asymptotically   On the
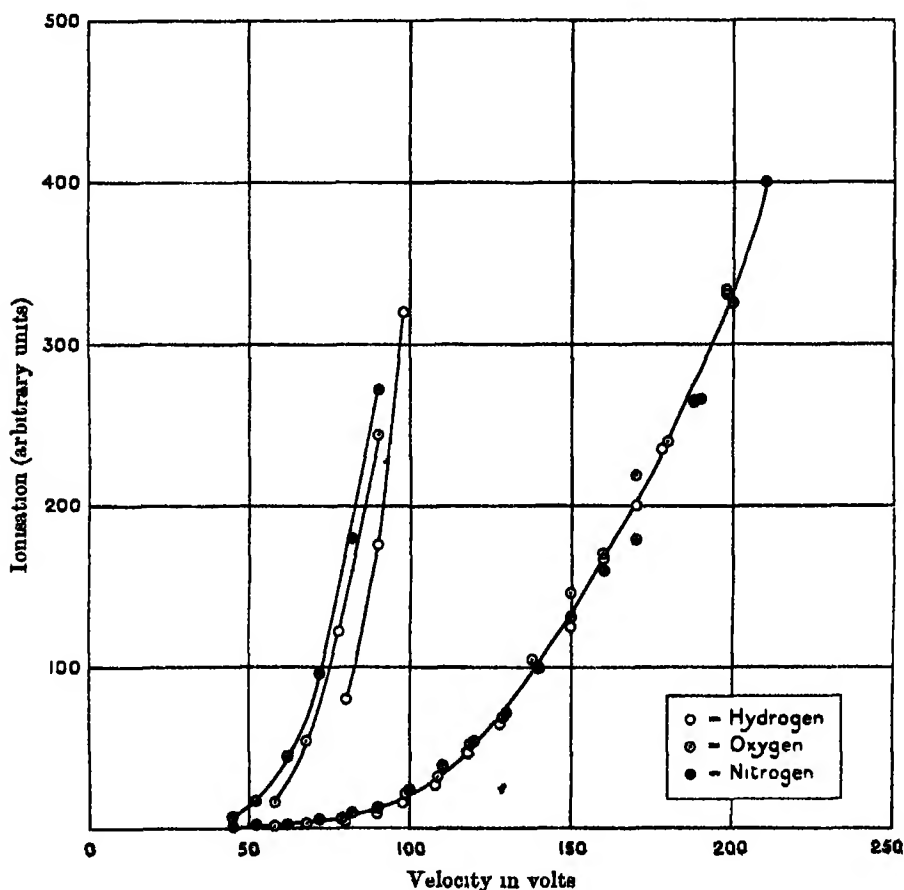

Fig 3

same fig 3 the beginnings of the curves are plotted on a larger scale, showing that the curves for O_2 and N_2 seem to go down a little less steeply than H_2 curve   It was of special interest to try to find the point at which these curves cut the axis of x.   For this purpose the intensity of the source of the positive ions was increased by making the platinum strip wider, coating it with fresh salt and heating it very strongly.   In this way it was possible to continue the curves to the x-axis   Fig. 4 gives an example of the

results obtained with hydrogen for three values of the heating current—
(1) 3 85 ampères, (2) 3 7 ampères, (3), 3 5 ampères It clearly shows that
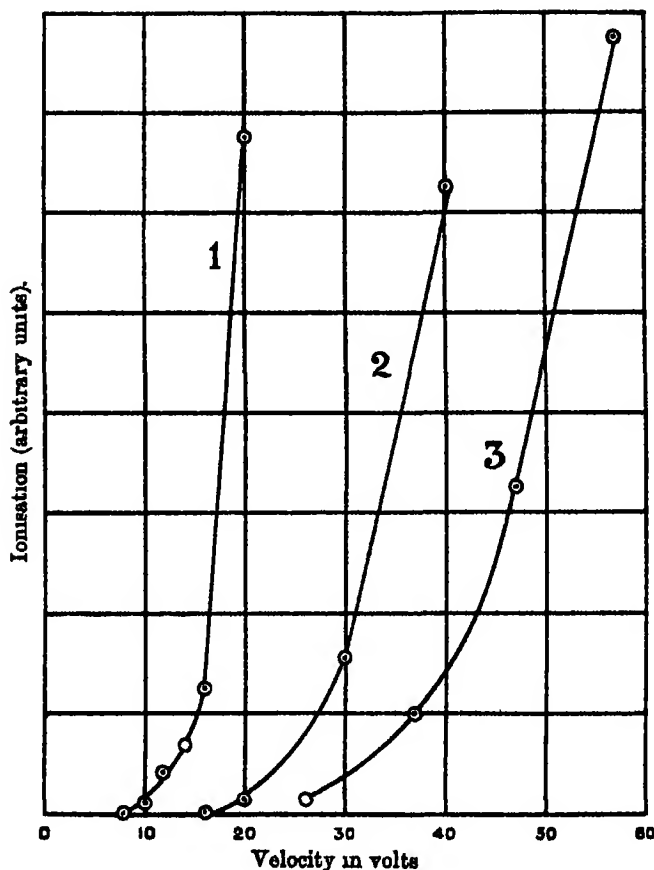the beginning of the curves actually depends upon the intensity of the

Fig 4

source of the positive ions and that it occurs in any case at a velocity lower
than 10 volts

One objection to the experimental arrangement here described is that as
the field accelerating the ions changed, the number of the emitted particles
no doubt changed also,* and therefore the asymptotic form of the curves
might be due as much to the decrease in the number of the ionising
agents themselves as to the decrease in the ionising power of the positive
ions with the decrease of their velocity In fact special measurements

* O W Richardson, 'Phil Trans,' A, vol. 207, p 40 (1906), F Horton, 'Roy. Soc
Proc,' A, vol 88, pp 121, 127, 133 (1913)

have shown that, even at these low pressures (0 0005 mm) and small distances (1 mm), the thermionic current from platinum coated with sodium phosphate does not show complete saturation, the first branch of the curve passes gradually into the second, which rises less steeply with the voltage   In order to diminish this change in the number of positive ions themselves, and have a more constant supply of them which would not depend so much upon the accelerating field, slight alterations were made in the form of apparatus and in the method of observation

The alteration is shown in fig 2   It consisted in introducing the platinum gauze R between the source of ions and the bottom of the ionisation chamber Throughout the experiment it had a small constant difference of potential with regard to the platinum strip P, and the accelerating force which was changed in the course of the observations was applied between the gauzes R and D   This small constant difference of potential between the strip P and the gauze R might be called, for brevity, "extracting" potential, to distinguish it from the difference of potential between R and D as "accelerating"   The total energy acquired by a particle is, of course, equal to the sum of both the "extracting" and the "accelerating" potential   There is no doubt that any change in the "accelerating" potential would still have a slight effect upon the number of ions extracted from the strip P, but it is in any case much less than in the first form of apparatus

The results of the experiments performed with this arrangement confirmed those which had been already obtained   The ionisation curves still preserve their characteristic shape, having the axis of x as asymptote

In the course of the previous experiments the negative potential of the ionisation chamber was gradually altered through the whole interval of voltage investigated   With this arrangement the possible existence of negative corpuscles inside the ionisation chamber due to any extraneous causes must be considered   If the actual ionisation inside the cylinder does not depend altogether upon the velocity of the positive ions, but is partly due, for instance, to some radiation emitted by the glass sides of the vessel under the impact of positive ions, or to some negative corpuscles which for any reason, penetrate into the ionisation chamber, or to the dissociation of heated salt vapour, the curves obtained would still be of the same general type   To avoid an error due to this possibility the following method of observation was adopted —The ionisation chamber, *i.e.* the cylinder D, was kept at the constant potential of − 207 volts during the whole time of observation.   Only the potentials of the gauze R and the strip P were changed, the difference between the two being kept fixed, for instance, at 20 volts—the "extracting" potential.   Under these

conditions the only variable was the velocity of the positive ions between R and D   The following table gives an idea of an actual series of observations and shows that any effects due to such extraneous causes as have been indicated would be too small to have any influence on the observations

Potential of the strip P	Potential of the gauze R	Potential of the cylinder D	Velocity of ions in volts	Ionisation current in arbitrary units
− 90	−110	−207	117	360
−100	−120	−207	107	230
−110	−130	−207	97	143
−120	−140	−207	87	93
−130	−150	−207	77	61
−140	−160	−207	67	29 5
−150	−170	−207	57	12
−160	−180	−207	47	5
−170	−190	−207	37	1 4
−180	−200	−207	27	0 5

§ 3 *Comparison of the Ionisation by Positive Ions and Negative Corpuscles*

The scheme described above was finally adopted for two purposes first, to compare the ionising action of positive and negative carriers of electricity emitted by hot salts and by heated platinum ,
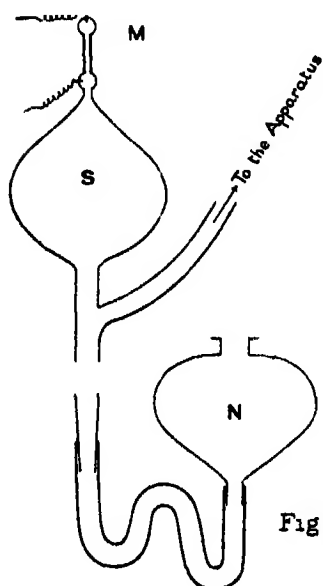

Fig 5

secondly, to measure the ionising potential for the negative corpuscles under conditions somewhat different from those used by Franck and Hertz * These experimenters found that the ionising potentials for H_2 and He are considerably different These gases were therefore used in the following research The hydrogen was prepared electrolytically and the helium by boiling powdered thorianite in nitric acid   It was carefully purified from possible impurities by passing it through tubes filled with charcoal and immersed in liquid air   During the whole experiment the apparatus was kept connected with the same charcoal tube In order to be quite sure of the purity of the gas filling the apparatus at such low pressures, a small Geissler tube was placed in connection with it   The side tube F (fig 1) led to a large glass vessel S, of which the narrow upper part

* J Franck and G Hertz, *loc cit.*

was closed by a small capillary Geissler tube M   By means of the movable mercury reservoir N which was connected as is shown in fig 5, the gas in the vessel S could be compressed to a small fraction of its initial volume This was necessary, because at the pressures used in these experiments (0 01–0 001 mm) a discharge sufficiently luminous to give a spectrum could not pass through the Geissler tube   The gas after standing for some hours in the apparatus in connection with a charcoal tube gave a strong spectrum of helium , the hydrogen lines were very faint

The curves 1 (H$_2$) and 2 (He) of fig 6 represent the results of the observations, the "extracting potential" being 8 volts in this case, O refers
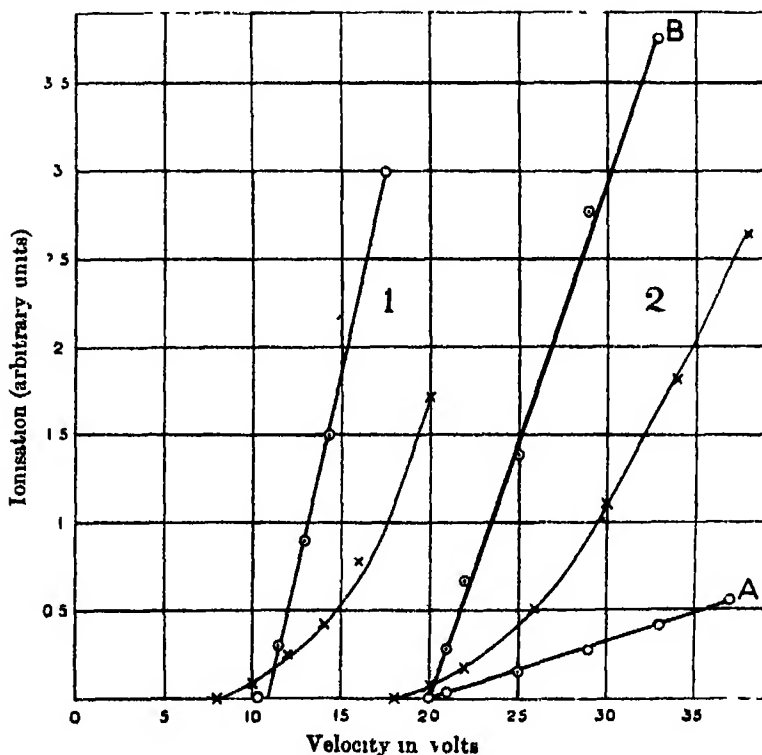

Velocity in volts
FIG 6

to negative corpuscles, × to positive ions   The main difference between the curves of the type ⊙ and the type × is clearly seen   For negative corpuscles they are very nearly straight lines, cutting the axis of x in definite points, corresponding to a velocity of 11 volts for H$_2$ and 20 volts for He   For positive ions they are curved lines, which in the present experiments also seem at first sight to cut the axis of x in a definite point, but probably only approach it.   The difference becomes more obvious if one

increases the intensity of the thermionic current by increasing the heating current In the case of negative corpuscles in He, on increasing the emission tenfold the straight line B was obtained, which cut the axis at the same point as A This point was very sharply defined, for the velocity of 21 volts the ionisation was measured by the movement of the gold leaf of the electroscope, the rate being 50 divisions in 30 seconds, while for the velocity 20 volts the rate was only 50 divisions in 10 minutes For the positive ions, as has been already mentioned, the effect of an increase of their number is, within the limits of the experiments, to shift the point of intersection of the curve with the axis of x towards the smaller values of velocities

§ 4 *Distribution of Velocities*

In order to be able to draw any definite conclusion as to the magnitude of the ionising potential, it was necessary to be sure that the actual distribution of electric force inside the apparatus corresponded to the potentials externally applied In other words it was necessary to investigate the actual distribution of velocities among the negative corpuscles and positive ions For this purpose an accelerating field was applied between the platinum strip P and the gauze R, and a retarding field between the latter and the bottom of the cylinder D The cylinder itself was connected to earth through a sensitive d'Arsonval galvanometer, which gave 1 mm deflection for a current 10^{-9} ampère The current was measured with a constant accelerating potential difference between P and R, while the retarding potential between R and D was gradually changed from zero till it was sufficiently strong to stop the whole current In the following an actual example is given —The strip P was charged to $+10$ volts, the gauze R was earthed, and the current carried by the positive ions to the cylinder D was measured by the galvanometer Then the strip was charged to $+9$ volts, the gauze to -1 volt, and the current measured again In this case the accelerating field was still 10 volts, but all the ions having a velocity below 1 volt were now stopped by the retarding field of 1 volt, and the current in consequence became a little smaller. Proceeding in this way, and increasing the retarding potential by equal steps of 1 volt, we finally reach the stage when the current is reduced to zero At one particular step the retarding potential produces a much greater diminution in the current than at any other. Since now the largest number of particles is stopped by this retarding potential, it is evident that the majority of the particles have a velocity slightly below that which corresponds to this value of retarding potential.

The Table contains the results obtained for both positive ions and negative corpuscles, with an accelerating field of 10 volts and 7·5 volts respectively.

Positive ions			Negative corpuscles		
Mean potential of the strip P	Potential of the gauze R = retarding potential	Current in percentage	Mean potential of the strip P	Potential of the gauze R = retarding potential	Current in percentage
+ 10	0	100	− 7 5	0	100
+ 9	−1	100	− 6 5	1	98 5
+ 8	−2	97	− 5 5	2	87 5
+ 7	−3	95	− 4 5	3	82 5
+ 6	−4	93	− 3 5	4	77
+ 5	−5	88	− 2 5	5	71
+ 4	−6	79	− 1 5	6	63 5
+ 3	−7	61	− 0 5	7	50
+ 2	−8	31 5	0	7 5	40
+ 1	−9	0	+ 0 5	8	23
			+ 1 5	8 5	10 5
			+ 2 5	9	2 6
			+ 3 5	10	0

Representing these numbers in the form of curves, and graphically differentiating them, it is quite easy to get the relative percentage of particles which corresponds to every velocity This is represented on fig. 7A and fig 7B, where the velocities in volts are taken as abscissæ and the

Positive ions.
Fig. 7A.

Negative corpuscles.
Fig. 7B.
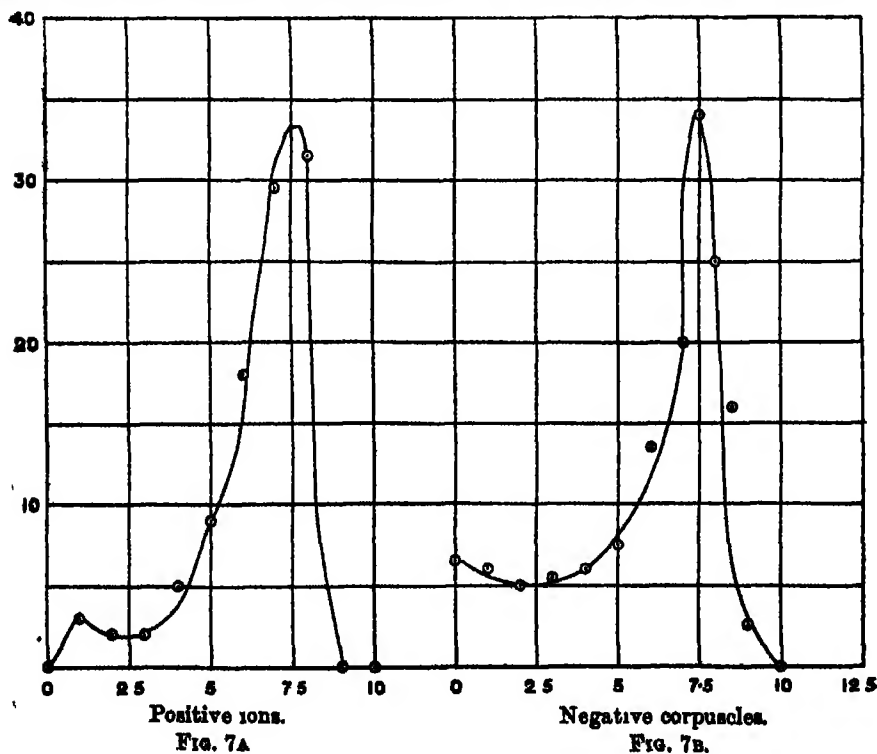
relative percentage of particles as ordinates It is seen that, in the case of
negative corpuscles, we deal with a source of particles of nearly homogeneous
velocity corresponding to the difference of potential actually applied From
this fact it follows that the intercept on the x-axis gives the absolute value
of the ionising potential for negative corpuscles In the case of the positive
ions the results are slightly different. The maximum number of particles
occurs at a velocity less than the velocity applied, and there are no particles
at all which possess the value of the applied velocity The distribution of
velocities for positive ions was investigated at various pressures and with
various applied velocities, less than 10 volts, but the same effect was always
observed Whatever may be the explanation of this fact, its influence on
the value of the ionising potential for positive ions is only to make that
potential still smaller than the value given by the curves

§ 5 *Action of Magnetic Field*

Finally, the action of a strong magnetic field on the positive emission and
on the ionisation was studied The experiments were carried out in the
following order The magnetic field might be applied between the strip P and
the gauze D (fig 1) At some definite velocity of the positive ions, for instance,
60 volts, the effect of the magnetic field on the magnitude of the thermionic
current passing to the cylinder D was measured In this particular case the
positive thermionic current was reduced to 80 per cent of its original value
by putting the magnetic field on In this case 20 per cent of the positive
ions were deflected from their path, so that they did not enter the cylinder D.
On measuring the ionisation produced in the cylinder by positive ions of the
same velocity, it was found that this also was reduced to about 80 per cent.
of its value by applying a magnetic field of the same intensity It is clear
that, if 20 per cent of the ionising agents are prevented by the magnetic
field from entering the cylinder, the ionisation ought also to be 20 per cent
less The intensity of the magnetic field was chosen so as to deflect
completely the negative emission, and, under these conditions, no ionisation
due to the negative corpuscles could be detected in the cylinder These
results may be taken as a fresh demonstration of the fact that there exists
an intimate connection between the number of positive ions and the
negative charge, observed in the ionisation chamber

§ 6 *Discussion of Results*

On examining the observations made and the results obtained we are led
to the definite conclusion that the negative charge observed in the ionisation
chamber depends only upon the presence in it of the positive ions and upon

these velocity   This power of the positive ions to produce a negative charge
in the gas can only be explained in two ways   We may suppose that a process
occurs analogous to that first observed by Wien[*] in the case of positive rays
in a discharge tube, i e that a change takes place in the electrical state of the
carriers themselves   The beam of positive ions may be in reality a mixture of
positive, negative and neutral particles which are in a state of statistical
equilibrium   The negative part is accelerated by the electric field inside the
ionisation chamber, and the negative charge observed on the electroscope in
this case would be carried by heavy negative ions   On the other view we
have to admit the formation of new ions and corpuscles by the collision of the
positive ions with molecules of the gas, i e we must admit ionisation by
collision at such unusually low velocities as those used in these experiments
In this case the negative charge observed in the ionisation chamber is carried
by corpuscles   The two points of view are not entirely different and it seems
that the first hypothesis may possibly include the second   As the experiments
of Sir J. J Thomson[†] have shown, the passage of positive rays through a gas
is always accompanied by a very strong ionisation of the gas in the tube   It
seems quite reasonable then to treat this ionisation as a primary effect and to
consider the neutralisation and the acquiring of a negative charge by a positive
particle as a secondary effect[‡]   On this view it is easier to understand how
the positive particles could combine with the negative corpuscles, which are
formed in the gas in the free state in the way explained   The charge actually
observed on the electroscope would thus be the sum of the charges on both
negative ions and negative corpuscles

Accepting the second point of view, we see that our results remove some
difficulties which arise in applying the theory of ionisation by collision to
the results of Townsend's[§] experiments   These experiments investigate the
change, with the distance between the plates, of the current due to photo-
electrons in the electric field and the conditions under which a spark is pro-
duced between the electrodes.   The difficulty is that, expressing his observa-
tions by a theoretical formula

$$n = n_0 \frac{(\alpha - \beta) e^{(\alpha - \beta)l}}{\alpha - \beta e^{(\alpha - \beta)l}},$$

[*] W Wien, 'Ann der Phys.' (4), vol, 27, p 1025 (1908)
[†] J J. Thomson, 'Phil Mag ' (6), vol 24, p 232 (1912).
[‡] See, however, W Wien, 'Ann. der Phys ' (4), vol 39, p 538 (1912)
[§] J S. Townsend, 'The Theory of Ionisation of Gases by Collision '

where *n* is the number of negative ions which reach the positive electrode,

   n_0 is the number of negative ions which start from the negative electrode,

   l is the distance between the electrodes, and

   α and *β* are the numbers of ions produced by negative and positive ions respectively in 1 cm distance,

though we get complete agreement with the experimental results, we are led to conclude that positive ions possess the power of ionisation even in comparatively low electric fields and at comparatively high pressures These last two conditions limit the energy acquired by the particles during their free path to a very small value, *i.e* make the ionising potential for positive ions very small—a fact which was not observed in *direct* experiments Now the result of the experiments described in this paper gives to this fact a direct experimental verification, proving that the energy required by a positive ion to ionise a molecule of a gas is of the same order as that required for this purpose by negative corpuscles Now in some of the present experiments a negative thermionic current about 10 times smaller than the positive one gave an ionisation about 10 times larger with equal velocity of the carriers of electricity in both cases The question thus arises · what is the cause of this difference between the ionising powers of negative corpuscles and positive ions ? It seems possible to answer the question in this way Within the range of velocities and pressures investigated here the collisions which result in the ionisation of a molecule of a gas occur much more often in the case of the negative corpuscles than in the case of positive ions This view is confirmed by Townsend's* values for the numbers *α* and *β* of ions produced in 1 cm distance by a negative corpuscle and by a positive ion For helium he gives *α* = 0·5 , *β* = 0 0095, *i e*, in the case of negative corpuscles 50 per cent of them make collisions which result in ionisation of the gas molecules, while in the case of positive ions only 1 per cent of them succeed in producing ionisation

§ 7 *Summary*

1. The property of positive ions to produce a negative charge in a gas has been investigated for a considerable range of velocities of the ions

2 It seems probable that the effect observed was due to ionisation by collision of positive ions

3 The results show that the ionising potential for positive ions in hydrogen is about 10 volts, which is of the same order of magnitude as

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* J. S. Townsend, *loc cit*, p 49.

the ionising potential for negative corpuscles, the positive ions being derived from heated salts

4 In a new experimental arrangement, measurements of the ionising potential for negative corpuscles were repeated, and the values, 11 volts for hydrogen and 20 volts for helium, were obtained, which confirm the results of Franck and Hertz

5 Observations were made on positive ions emitted by heated sodium phosphate in hydrogen, oxygen, nitrogen, and helium

Further experiments are in progress   When this research had been conducted to the point described above, a paper by E v Bahr and J Franck appeared in the ' Verhandlungen der Deutschen Physikalischen Gesellschaft,' January, 1914, which contains results which are in agreement with those of the experiments described in § 2 of the present investigation

The author gladly takes this opportunity of thanking Prof Sir J J. Thomson for his kind permission to carry on this research in the Cavendish Laboratory, and for the interest he has taken in the investigation

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The Determination of Fatigue Limits under Alternating Stress Conditions.

By C E STROMEYER

In the year 1867 A Wohler, locomotive superintendent of a railway company in Berlin, exhibited at the Paris Exhibition the results of some experiments on the endurance of metals, and was thereupon engaged by the Prussian Government to carry out the more exhaustive enquiry into this subject with which his name is always associated   The results of his labours were published in 1871, and were highly appreciated, but few additional experiments were made until the subject was again taken up successively by Sir Benjamin Baker, Reynolds and Smith, Rogers, Stanton and Bairstow, Eden, Rose and Cunningham, and Prof. Hopkinson   All these experiments are confined either to fatigue bending or to push and pull tests, using only steel or iron, whereas the present ones include a large number of torsion fatigue tests on various metals

Until comparatively recently there was no satisfactory standard of comparison for fatigue tests, the determination of the asymptotic or limiting fatigue stress for an infinite number of revolutions from a few irregular test results leading to very uncertain conclusions, so much so that by some it was considered very doubtful whether there were any real fatigue limits, while others adopted as standards of comparison the fatigue stresses which would cause fractures at the millionth repetition   The first problem which had to be investigated was therefore to ascertain the relationship between the intensities of fatigue stresses and the numbers of repetitions of these stresses which would cause fracture, and, should this relationship be found to indicate the existence of a limiting stress for an infinite number of revolutions, or more briefly of a fatigue limit, then the next step would have to be its exact determination

A discussion of Wöhler's tests, which has often been attempted, did not seem to be likely to lead to any definite results, for he was evidently under the impression that the quality of steel with which he was being supplied by several steel makers did not vary during a twelvemonth, and instead of making a series of tests with small samples cut from a single axle, he seems to have made his test-pieces so large that a separate axle had to be used for each one, although the first may have been supplied in January and the other in December of a single year   Since his days it has become known that, even in a single ingot, comparatively large differences exist as regards chemical composition and mechanical properties, according as to whether the samples are taken from near the surfaces of the ingots or from the tops or bottoms of their cores   Therefore, in order to reduce to a minimum the chances of obtaining irregular fatigue results, the author made use of very short test-pieces, so that the distance from sample to sample did not exceed 3 inches and for the bending tests was as small as 1 inch   The shape of the samples used for bending fatigue tests is shown in fig 1, each test-piece consisting of
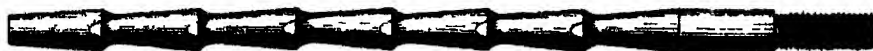

Fig 1.

seven waists and cones. The end cone of each sample was firmly inserted into the socket of a horizontal revolving spindle (fig 2), and to the other end of the test-piece was screwed a hardened steel rod from which a weight was suspended   After revolving the spindle for a certain number of times the first (left hand) waist would break and the second cone would be inserted in the socket, and so on until all the waists were broken. The load on the end of the bar was not altered, so that the bending moment on any one waist

would be the same throughout the entire duration of the test   With this form of test-piece the six successive fractures would be separated from each other by only 1 inch

With the permission of Prof Dalby, his assistant, Mr (now Professor) A. J Margetson, carried out a series of bending fatigue tests during 1907
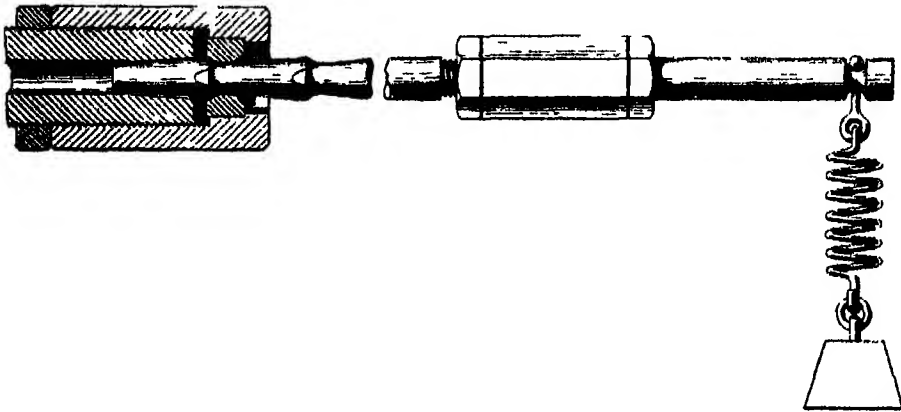
Fig 2

and 1908 on about 30 different qualities of steel, of which a large number had been cut from plates which had failed in practice   His results have been carefully analysed and were found to comply with the empirical condition

$$\pm S_n = Fl + C\,(10^6/N)^{1/4},$$

where Fl is the extrapolated fatigue limit, C is a coefficient affecting the endurance under severer stresses, and $\pm S_n$ is the nominal fatigue stress which will cause rupture if repeated N times, N being the total number of stress cycles or revolutions up to fracture.   The nominal fatigue stresses $\pm S_n$ are calculated from the alternate bending moments as if the material were perfectly elastic up to these stresses, whereas, on account of the plasticity of steel under severe stresses, the actual fatigue stresses are necessarily lower than these nominal ones, except for vanishing differences of $S_n - Fl$ The correction for reducing S_n to S will therefore most likely not affect Fl, the exterpolated fatigue limit, which is the main object of the present enquiry, but it will certainly affect the coefficient C and, possibly, also the index 1/4.

The results of these bending tests have been recorded diagrammatically in figs. 3 and 4, the vertical scales of the diagrams representing the nominal bending fatigue stresses $\pm S_n$, and the horizontal ones representing the expression $(10^6/N)^{1/4}$ Seeing that the distance which separates the first
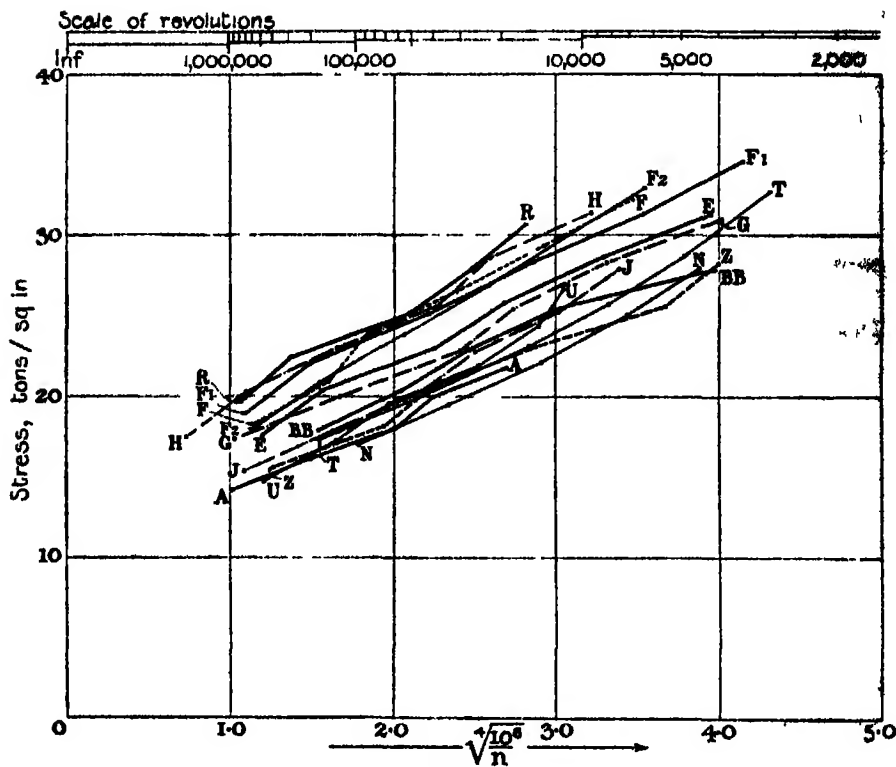
Fɪɢ 3

fractured waist from the last (see fig 1) is only 6 inches, it was hoped that, within this length, no change of endurance qualities would occur, and that the intersections of the prolongations of the plotted test results with the zero ordinate might be looked upon as being the true fatigue limits, but, judging by some of Messrs. Eden, Rose, and Cunningham's test results, very marked changes of endurance qualities are met with even in short lengths of rods, and with the form of test-piece adopted in the present trial, these local changes would introduce systematic errors, either altering the slopes of the lines in figs 3 and 4 or curving them, and these influences would indirectly affect the extrapolated fatigue limits Fl. Partly for this reason, partly because of the exceptional chemical compositions of the steels marked D and F, these were subsequently tested in duplicate and the results are as follows :—

     Sample D.....   .   Fl = 10·92 and 12·79.,   C = 3·78 and 3·74.
     Sample F.   ....   Fl = 11 49, 11·75 and 14 33;   C = 5 98, 6·02, 4·85.

These agreements and disagreements could easily be explained by assuming certain slight local differences of endurance qualities, but as they indicate
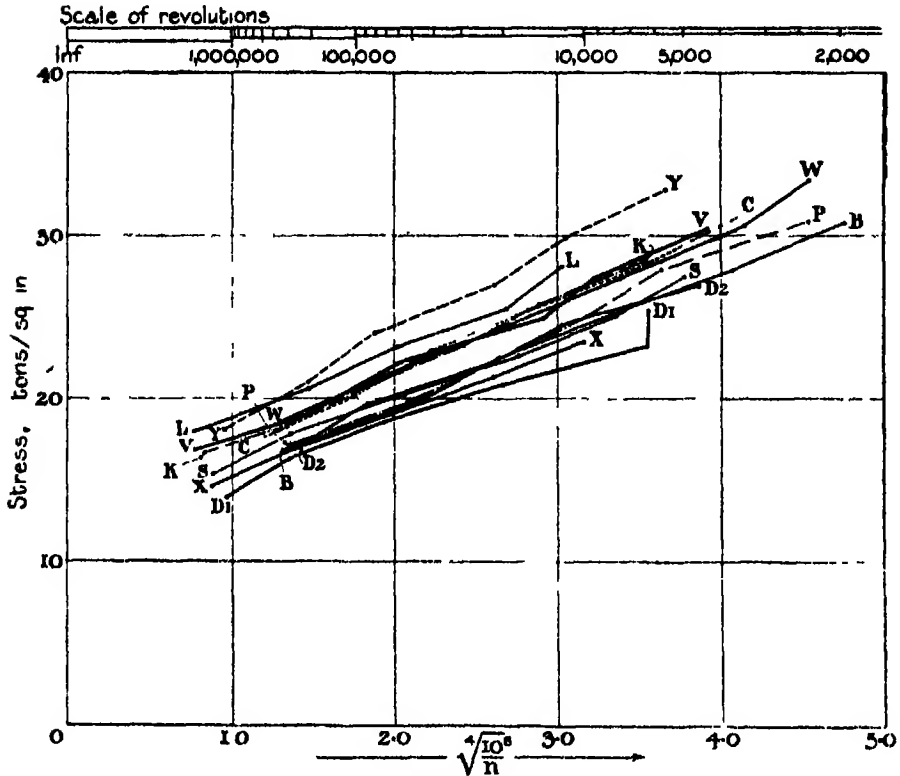
Fig 4

that a considerable amount of uncertainty attaches to extrapolated fatigue limits, they may be taken as a thorough justification for the carrying out of further tests which had for their object the direct determination of fatigue limits, therefore the Committee of the Manchester Steam Users' Association for the Prevention of Boiler Explosions very kindly sanctioned the construction of a fatigue testing machine, and, more recently, of an improved one with which these determinations could be made by means of a calorimetric method, which is described below.

Seeing that Wohler had made only two satisfactory torsion fatigue tests, and seeing that none have been made since his days, whereas bending fatigue tests have been fairly numerous, a torsion fatigue testing machine was decided upon for the additional work. Its essential feature is the transmission of alternating torsion moments from a rocking crank through a test-piece to a fairly heavy flywheel. The intensities of these moments and of the alternating nominal shearing stresses $\pm S_n$ in the test-piece were estimated from the known moment of inertia and the number and amplitude of the oscillations of the flywheel W, while the number N of stress cycles

2 G 2

was recorded by counters The testing machine is illustrated in fig 5 (elevation) and fig 6 (plan)

SccS is the central crankshaft with a heavy flywheel F, which gives steadiness of rotary motion It is driven at about 600 revolutions per minute by a belt from the motor M The throw or double radius of each
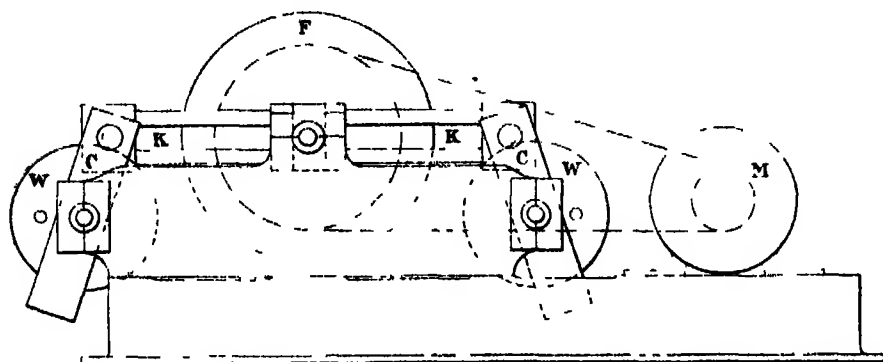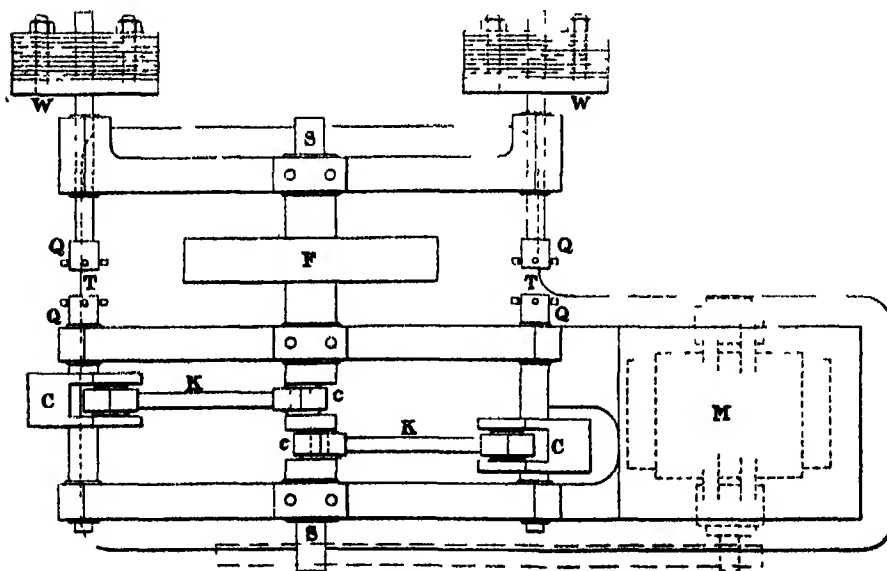

Fig 5 —Elevation

Fig 6 —Plan

crank is 1 inch Two connecting rods KK join the rotating cranks *cc* to the balanced rocking cranks CC, whose radii of action are 4 inches. The shafts of these cranks end in clutches QQ, and the spindles of the two flywheels WW have similar clutches, into which the ends of the test-pieces TT can be secured The flywheels WW are built up of a number of circular

discs, whose moments of inertia have been accurately determined   The cranks CC are, as will be seen, inclined at angles of about $22\frac{1}{2}°$, which angles can be slightly altered by adjusting the lengths of the connecting rods KK   This inclination of the cranks CC is an essential feature of the machine, for without it the torsion moments would not be equal at both ends of the stroke, and the test-pieces would acquire increasing twists in one direction while the test is in progress

The shapes of the test-pieces held by the clutches QQ, and the attachments for the calorimetric measurements are shown in fig 7   For the latter purpose the test-piece T is surrounded by a thick indiarubber sleeve, shown in section, to which an inlet and an outlet pipe are cemented, sensitive thermometers t_1 and t_2 being placed in each pipe   A steady stream of water enters at I, its temperature being read off at t_1, it travels along the test-piece T, taking up any heat which may be generated in it, and passes out at O, the discharge temperature being recorded by t_2 When much heat is generated in a test-piece a small portion escapes through the clutches QQ (fig 6), because these would be relatively cold, and if the clutches are warmer than the test-piece heat will travel into it   In order to determine the amount of this conducted heat, holes were drilled into the bearings near QQ and thermometers inserted, whereby the flow of heat from or to T was determined in terms of the difference of temperature between that of the test-piece and the two bearings.   The flow of the cooling water was maintained at a very steady rate by a constant head of pressure, and was frequently checked   It could be reduced to 2 c c per minute, and as the temperature could be read to $0\,01°$ C, the calorimetric attachment would be capable of just indicating $0\,02$ small calories per minute, or $1\,43$ grm -cm. of work per revolution or stress cycle, of which there were about 600 per minute   This plastic work is represented in fig 8 by the area of the
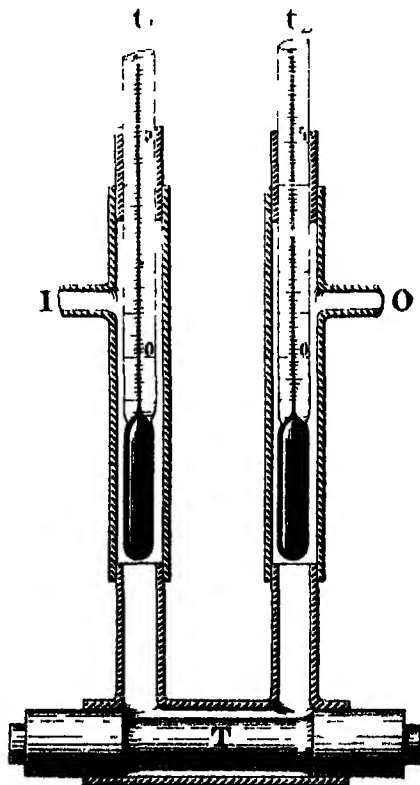

Fig 7

loop *abcd*, OF being the maximum twisting moment and F*b* the twisting angle of the test-piece   For test-pieces of the dimensions used in these experiments the elastic work, if added together for each quarter cycle, or twice the product OF × F*b*, was from 1000 to 3000 times larger than the area *abcd*
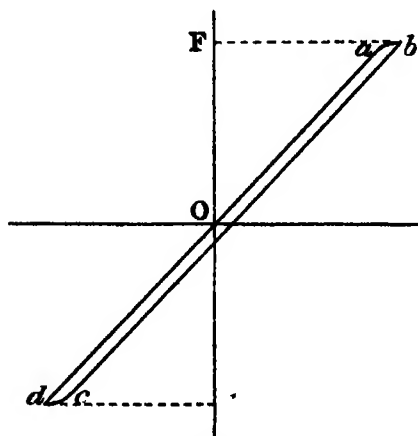
In the present experiments the accuracy was reduced to about 1 per cent by increasing the flow of water to about 30 c c and by disregarding differences of temperatures of less than 0 02° C

Before proceeding with the calorimetric determination of fatigue limits, it was deemed desirable to subject all the samples, of which the bending fatigue tests are recorded in diagrams 3
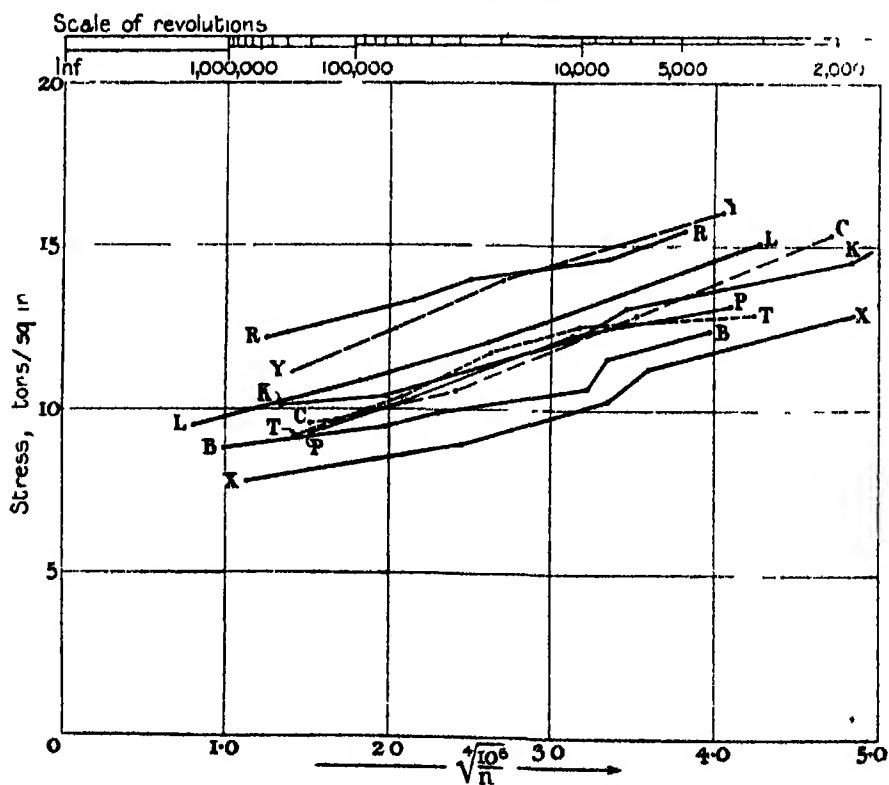
Fig 8

Fig 9

and 4, to torsion fatigue tests, using waisted samples of the very shortest dimensions (1½ inch over all)   The experiments were mostly carried out by my assistant, Mr H A. Jones, B Sc , and the results are recorded diagrammatically in figs 9 and 10, which are arranged on the same plan as diagrams 3
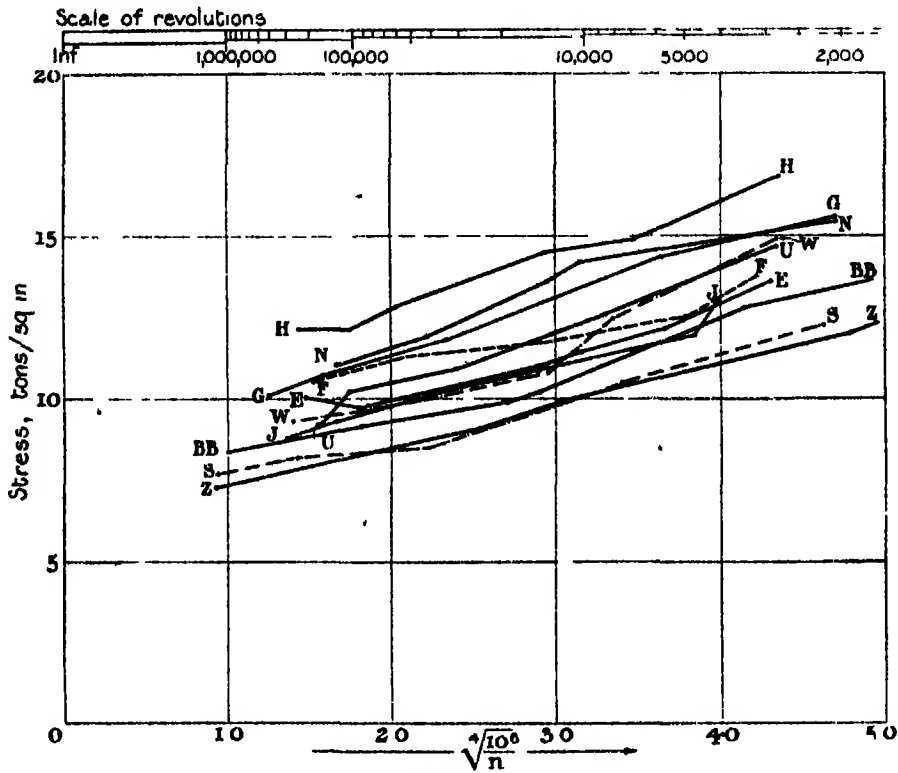
Fig 10

and 4, except that the vertical scales (stresses) are twice as large as the previous ones   As will be seen these plotted torsion fatigue test results lie on practically straight lines, which is an indication that a definite fatigue limit also exists for torsion fatigue stresses, and should be sought for where the prolongations of the several lines cut the zero ordinate

It may here be mentioned that the extrapolated fatigue limits for torsion (shear) average two-thirds of those for bending, and that the coefficients C for torsion average 0 3 of those for bending, but individual ratios differ from the means up to about ±25 per cent   All the previous tests had been made on bars cut from plates, but as some of these plates showed laminar segregations, which may have affected the results, all the subsequent tests have been made with samples cut from rolled bars.

The calorimetrically determined fatigue limit is that minimum alternating stress which will just generate heat in the test-piece This generation of heat is almost certainly an indication that the material of the test-piece is being fatigued by being alternatingly stressed beyond its elastic limit, and that if the process could be continued an infinite number of times the test-piece would fracture But in the previously mentioned empirical formula $\pm S_n = Fl + C(10^6/N)^{1/4}$ the fatigue limit Fl is found by extrapolating those alternating stresses which result in actual fractures, which limit is therefore that stress which will cause fracture if repeated an infinite number of times, and if this empirical formula should be applicable to an infinite number (N) of stress cycles, then the fatigue limit as found calorimetrically in a test of short duration should agree reasonably well with it In order to clear up this point five bars were tested—LA, LB, LD, LE, LF—and the results recorded in Table I and in diagram 11.

As will be seen, the agreement between the two methods of testing is a remarkably close one, the stresses, as estimated from the observed number of
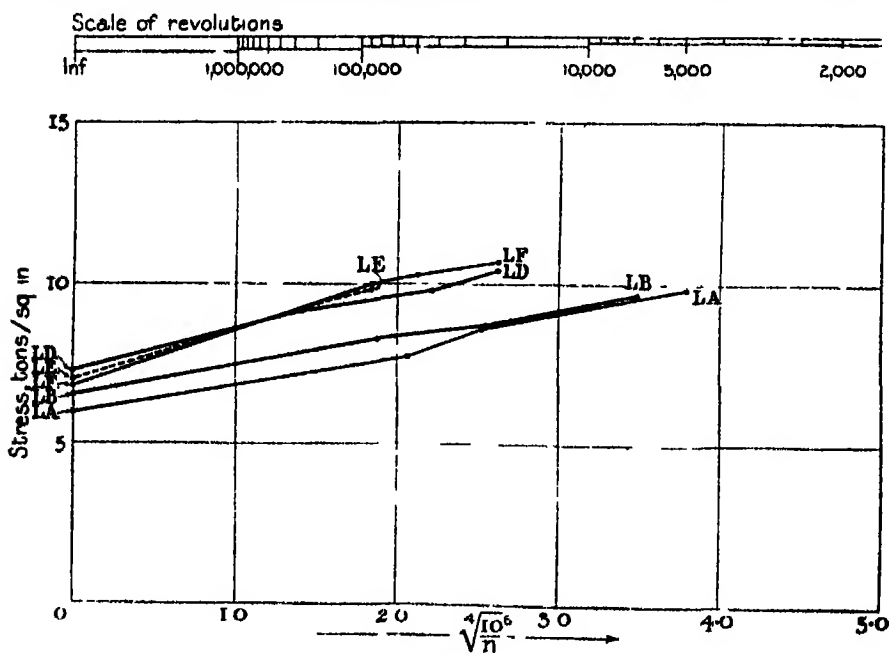

Fig 11.

revolutions, agreeing with the applied stresses more closely than might have been expected from the irregularities of the curves in Diagrams 3, 4, 9, 10. The worst case is LF, for which the differences are —0 52 and +0·60 ton per square inch, but these could be nearly eliminated if in the formula

Table I —Comparative Torsion Fatigue Tests

Sample mark	Fl, calorimetric	±S_n, fatigue stresses	N, revolutions to fracture	(10^6 N$^{1/4}$)	Fatigue stresses Estimated	Differences
	Tons per square inch				Tons per square inch	
Basic Open Hearth Mild Steel Bar						
LA 21	6 15	9 85	4,840	3 790	9 67	+0 18
LA 19	6 00	8 55	23,240	2 560	8 47	+0 08
LA 20	5 75	7 70	50,400	2 5	7 97	−0 27
Mean	5 97		(Mean coefficient, C = 0 977)			
Basic Open Hearth Mild Steel Bar						
LB 5	6 60	9 70	6,870	3 478	9 57	+0 13
LB 6	6 50	8 62	23,027	2 550	8 77	−0 15
LB 7	6 50	8 20	82,100	1 867	8 16	+0 04
Mean	6 53		(Mean coefficient, C = 0 701)			
Basic Open Hearth Mild Steel Bar						
LD 6	7 30	10 40	21,440	2 615	10 43	−0 03
LD 5	7 10	9 80	37,515	2 272	10 01	−0 21
LD 7	7 25	9 18	242,000	1 426	8 97	+0 21
Mean	7 22		(Mean coefficient, C = 1 225)			
Basic Bessemer Mild Steel Bar.						
LE 19	6 96	10 04	91,035	1 820	9 94	+0 10
LE 17	7 00	9 76	99,900	1 777	9 87	−0 11
LE 18	6 95	9 72	123,800	1 684	9 71	+0 01
Mean	6 97		(Mean coefficient, C = 1 680)			
Basic Bessemer Mild Steel Bar						
LF 18	6 88	10 70	21,200	2 620	11 22	−0 52
LF 19	6 94	10 30	49,800	2 124	10 89	−0 09
LF 17	6 67	9 92	206,600	1 484	9 32	+0 60
Mean	6 88		(Mean coefficient, C = 1 675)			

$\pm S_n = \mathrm{Fl} + \mathrm{C}(10^6/N)^{1/4}$ the index 1/4 were replaced by a smaller fraction. It is, however, probable that these discrepancies are due to irregularities in the material. Probably the most important result revealed by these experiments is the definiteness of the calorimetrically determined fatigue limits, the maximum differences from any of the mean values in Table I not exceeding 0 22 ton per square inch This result will appear all the more satisfactory when it is remembered that the static elastic limits for mild steel are such very uncertain quantities that engineers refuse to recognise them as being of any practical value, and prefer to judge of the qualities of mild steels by their ultimate tenacities, although these may vary by more than ± 5 per cent. in a single plate This definiteness of the fatigue limit was confirmed in a most gratifying manner by tests of 19 samples cut from a single crankshaft. Of these, three were cut from the scrap end of the shaft, probably near its surface, and the fatigue limits were found to be 11 15, 11 40, and 11 25 tons per square inch (11 27 mean). Eight other samples were cut longitudinally from the centres of the four crank webs close to the crank pins Their fatigue limits were 12 15, 12·05, 12 10, 12·10, 12·15, 12 00, 12 15, 12 05 tons per square inch (12 09 mean) Eight other samples were cut from the same positions, but across the grain; the results were 12·15, 11 30, 11·60, 11 30, 11·60, 11 35, 12 00, 11 30 The maximum difference between the mean and individual results were respectively 0 13, 0 09, and 0 57 ton per square inch, which is a most satisfactory result.

The calorimetric method of determining fatigue limits is not only simple and expeditious, but, as the above tests seem to indicate, also reliable, and may possibly help to throw new light on several as yet unsolved problems of mechanics, more especially if, as can easily be done by fracturing the sample, the coefficient C is also determined, which gives some indication as to the power of the material to withstand a few severe alternating stresses The rate of heat evolution during the fatiguing process has as yet not been correlated to any mechanical properties of the materials tested, but there seems to be a rough relation to the fatigue stress. Thus, for three mild steels, two cast steels, and aluminium, the ratio of the heat H evolved during the early portions of the fatiguing processes to the square of the ratio of the excess stress over the fatigue limit $(S_n - \mathrm{Fl})$ to the fatigue limit Fl, viz, $H \div [\mathrm{Fl}/(S_n - \mathrm{Fl})]^2$, is reasonably constant for each material, and the extreme mean values of C for such different materials as steel and aluminium are comprised within the limits of 329 and 548 (see Table II).

Table II —Fatigue Stresses and Rate of Evolution of Heat

Sample	ϕ Ratio of excess of stress over fatigue limit to fatigue limit $(S_n - F1)/F1$	H Heat evolved per minute per cubic inch of sample			Ratios	
		Initial stage		Mean		
		H_1 From	H_2 To	H_3	H_3/ϕ^2	H_3/ϕ^2
		inch pounds				
Three Samples of Mild Steel						
LA 20	0 323	20	60	66	575	638
LA 19	0 427	15	95	95	522	522
LA 21	0 ·620	200	210	260	547	677
Mean	—	—	—	—	548	611
LB 7	0 260	7	30	56	444	830
LB 6	0 325	0	50	118	474	1120
LB 5	0 475	87	110	243	488	1080
Mean	—	—	—	—	469	1010
LD 7	0 267	0	17	43	239	604
LD 5	0 374	0	72	125	516	898
LD 6	0 430	34	55	181	298	980
Mean	—	—	—	—	351	827
Two Samples of Cast Steel						
AA 3	0 430	0	21	33	114	179
AA 1	0 607	70	160	131	434	355
AA 2	0 795	105	220	273	349	432
Mean (omitting AA 3)	—	—	—	—	391	393
AB 1	0 ·441	0	52	57	267	293
AB 2	0 573	120	145	134	442	409
AB 3	0 ·744	65	165	179	299	324
Mean	—	—	—	—	336	335

Table II—*continued*

Sample	ϕ Ratio of excess of stress over fatigue limit to fatigue limit $(S_n - Fl)/Fl$	H Heat evolved per minute per cubic inch of sample			Ratios	
		Initial stage		Mean		
		H_1 From	H_2 To	H_3	H_2/ϕ^2	H_3/ϕ^2
		inch pounds				
One Sample of Aluminium						
AL 3	0 086	1 4	2 7	2 1	367	284
AL 1	0 154	3 3	5 7	4 9	241	207
AL 2	0 313	0 5	87 0	23 6	378	242
Mean	—	—	—	—	329	244

Having established the existence of definite fatigue limits for mild steel, additional torsion fatigue tests were made with other materials, the results being recorded in Table III and diagrammatically in fig 12. The latter shows very clearly that the endurance qualities of the tested metals can be expressed by the same formula as that which was found applicable to steel, and that each metal has a well marked fatigue limit

A knowledge of the true value of the fatigue limit of a metal will permit of greater exactitude being attained in the fixing of safe working stresses

Table III —Torsion Fatigue Limits Fl, and Coefficients C

Materials and sample marks		Fl, tons per square inch	C
A A	Tool steel	7 03	1 91
F 5108	"Era" manganese steel	10 40	1 96
F 5109	"Era" manganese steel	11 10	2 42
F 5113	Manganese steel, 14 per cent Mn	10 25	1 026
F 5114	Manganese steel, 10 5 per cent Mn	9 60	1 354
F 5117	Chrome nickel steel, 12 6 per cent Ni	12 60	0 504
FAR	Farnley iron	6 00	0 615
CI	Cast iron	3 98	1 61
NI	Pure rolled nickel	6 22	1 42 to 2 24
CU.	Commercial copper	5 50	0 44
P B	Phosphor bronze	7 82	0 72
AL	Rolled aluminium	2 16	0 127
MA	Rolled magnalium	4 22	0 077

Scale of revolutions
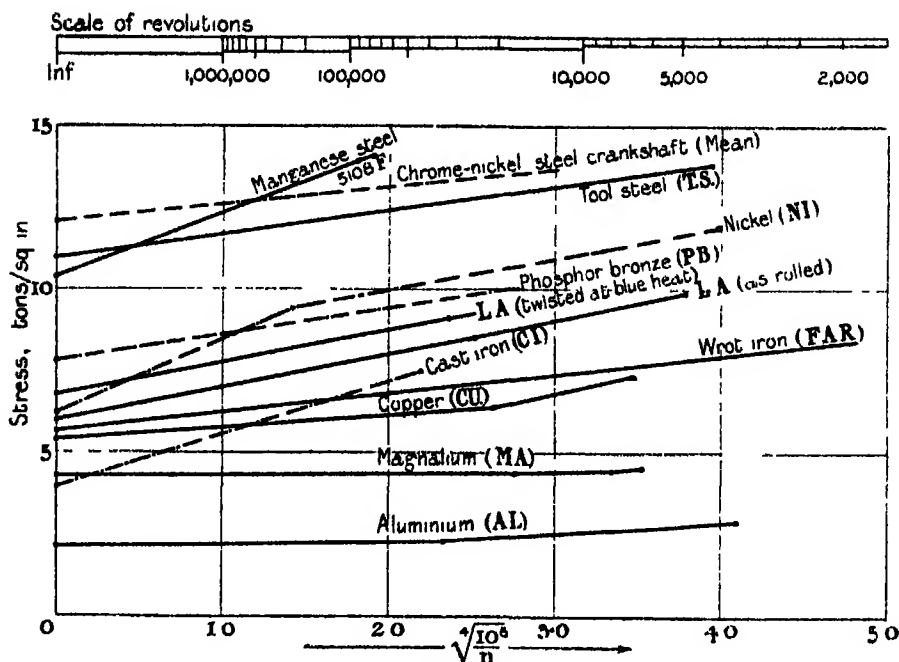

Fig 12

than is possible when only the ultimate tenacity is known   A knowledge of the relationship between the intensities of fatigue stresses and the numbers of their repetitions will also prove of value in enquiries into the cause of fractures   It has already been of great service in the determination of the stresses which caused a number of copper steam pipes of marine engines to fracture, and may be used for a similar purpose with regard to failures of crankshafts and railway axles

In conclusion, I beg to thank Prof Dalby, Prof A J Margetson, and Mr. H. A Jones for their valuable assistance, and those metallurgists who kindly supplied some of the samples, and especially do I wish to thank the Committee of the Manchester Steam Users' Association for their encouragement of the present and future researches.

BAKERIAN LECTURE : *Series Lines in Spark Spectra.*

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(Lecture delivered April 2,—MS received April 20, 1914)

(Abstract)

The classical work of Rydberg, and that of Kayser and Runge, dealt chiefly with series lines occurring in spectra which are produced in the electric arc, or in vacuum tubes with discharges of moderate intensity. In the present communication the lines considered are some of those which are specially developed in the condensed spark , that is, lines which belong to the class of "enhanced lines" as defined by Lockyer

The investigation was undertaken in connection with the new lines (λ 4686, etc) which were produced in 1912 by passing strong discharges through helium tubes, which always contained an impurity of hydrogen [*] These lines are of great interest in celestial spectroscopy, and, following Rydberg, they were at first attributed to hydrogen, they appeared to be closely related to the hydrogen series, while showing no relation to the known series of helium. In addition to the lines calculated by Rydberg for the "Principal" series of hydrogen, however, the "4686" series included an intermediate series which the recognised formulæ suggested was a second "Principal" series, having a simple relation to the first As the lines could not be obtained from hydrogen alone, it was soon felt that further enquiry should be made as to the value of the numerical evidence on which their assignment to hydrogen was chiefly based A search for other series of similar character was therefore instituted in the hope that some generalisation with regard to them might be reached

The conditions of appearance of the lines in helium tubes suggested spark spectra as the most promising source of such series, and a subsequent investigation of magnesium showed that the well-known spark line λ 4481 was the first member of a series of the kind looked for. No satisfactory evidence of relation to other series of magnesium was then obtained, and it seemed possible that both the "4686" and the "4481" series might be of a new type, having no necessarily simple relation to other series in the respective spectra.[†]

The lines of the "4686" series, and the associated "Pickering" series, have

[*] 'Monthly Notices Roy Astro. Soc.,' vol 73, p. 62 (December, 1912).
[†] 'Roy Soc Proc.,' A, vol. 89, p. 133 (June, 1913).

since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical investigations of Dr Bohr, who explains them as being produced during the first stage in the re-formation of atoms of helium from which both electrons have been removed by the strong discharges employed   Bohr's formula for this series is identical, in a first approximation, with that for hydrogen, except that the Rydberg constant N (= 109,675 for Rowland's scale) has four times its usual value   The two " Principal " series previously assigned to hydrogen were thus united in a single series of a new type, while the Pickering series was made to include additional lines nearly coincident with the Balmer series of hydrogen   It therefore became important to ascertain if such a modified formula could be adapted to the analogous " 4481 " series of magnesium, and to other series of spark lines if they could be found.

Further investigation of magnesium was also suggested by Dr. King's discovery that the line 4481 is a very close doublet   Two additional members of this series were resolved, and it at once appeared that the series was not of the ordinary Principal type   The new measurements also showed that the eight observed lines could be united in a single series of the new type suggested by the work of Dr Bohr   Other series of the same kind were found in Lyman's observations of certain " narrow " doublets in the spectra of calcium, strontium, and barium in the Schumann region

At this stage a valuable contribution to the investigation was made by the work of E Lorenser,[*] who had discussed the Lyman lines, and had shown that they formed series of the Fundamental (or " Bergmann ") type, associated with the wider doublets which occur in the spectra of these elements. Lorenser does not appear to have recognised that the lines in question belong to the special class of enhanced lines, but his work proved that these lines form a new class of series, and that similar groups of series occur both in arc and spark spectra.   The formula employed by Lorenser was of a modified Rydberg form, but further calculations have shown that the individual series, and the relation between the different series of the same element, are better represented by the Hicks formula with 4N for numerator.   One peculiarity of these series is that the first pair of the Diffuse series occurs with a negative sign in the formulæ, whereas it appears in arc series as a positive term

The wider doublets which occur in the spectrum of magnesium are in several respects analogous to the wider doublets of calcium, strontium, and barium, but the negative term of the Diffuse series is lacking, and a Fundamental series which would fall in line with those of the other three elements is also wanting.   The use of the Hicks formula shows that the

* 'Dissertation,' Tübingen, 1913.

lımıt of the "4481" serıes ıs related to the first *posıtıve* term of the Dıffuse serıes, but the fact that the doublets uccur both ın arc and spark, whıle 4481 requıres spark condıtıons, ındıcates that the relatıon ıs probably ındırect

The character of the spark serıes system of magnesıum has been elucıdated by the dıscovery of a new group of serıes of narrow doublets, whıch occur under exactly the same experımental condıtıons as 4481   Two of these paırs were observed by Fowler and Payn ın 1903, and for con-venıence of reference the new group uf serıes has been desıgnated the "FP" system   It ıs shown that the "4481" serıes ıs the Fundamental serıes of thıs group, ıts lımıt beıng derıved from the first negatıve term of the Dıffuse serıes, as ın the case of calcıum, strontıum, and barıum   There ıs evıdence that correspondıng serıes ın the "FP" and wıde doublet systems run parallel to each other, so that data lackıng ın one may be obtaıned from observatıons of the other   Thus ıt ıs found that the separatıon of the "FP" doublets ıs equal to the calculated separatıon of the *second* Prıncıpal paır of the wıde doublets, whıch lıes ın the Schumann regıon and has not yet been observed   Two well-defined combınatıon serıes, each consıstıng of seven lınes, have also been recognısed ın the course of the experıments on magnesıum, one derıved from terms of the Dıffuse and "4481" serıes, and the other entırely from the "4481" serıes

From these ınvestıgatıons ıt follows that two kınds of serıes have now to be recognısed   (1) serıes of the "arc" type, havıng Rydberg's N for the serıes constant, and (2) serıes of the 'spark" or "enhanced lıne" type, havıng a serıes constant equal to 4N   No numerıcal relatıons have yet been traced between the two sets of serıes occurrıng ın the spectrum of the same element.

Returnıng to the lınes produced ın helıum tubes, ıt ıs now clear that the lıne 4686 and the other lınes assocıated wıth ıt form a sıngle serıes of the enhanced lıne (4N) type, and that they can no longer be consıdered to belong to the same group as the Balmer serıes of hydrogen, whıch ıs of the arc (N) type   The close numerıcal relatıons ındıcated by Rydberg's calculatıons are therefore not sıgnıficant, and, ın vıew of the experımental evıdence, ıt must be concluded that the "4686" serıes ıs not due to hydrogen but to helıum, as first suggested by Dr Bohr from theoretıcal consıderatıons.   In accordance wıth the convenıent nomenclature of Lockyer, they may be desıgnated "proto-helıum" lınes   Analogy wıth the "4481" serıes of magnesıum suggests that the "4686" serıes ıs prımarıly of the Fundamental type, whıle the three assocıated serıes may be consıdered to be coıncıdent wıth ıt.

If the Pıckerıng lınes are also due to proto-helıum, as seems probable, the serıes must ınclude addıtıonal lınes whıch are almost superposed on the

Balmer series. Experimental and astronomical evidence on this point is incomplete, but there is no evidence against this supposition The assignment of the Pickering lines to proto-helium is supported by the observations of magnesium, since one of the new combination series is related to the "4481" series in exactly the same way that the extended Pickering series would be related to the "4686" series.

The close relations between the lines of hydrogen (real and hypothetical) and some of those of proto-helium is simply accounted for by Bohr's theory of the origin of these spectra. The formulæ, in which p and m can only take integral values, may be written—

$$\text{Hydrogen} \quad . \quad n = N\left(\frac{1}{p^2} - \frac{1}{m^2}\right) \quad p = 2 \text{ for Balmer series}$$

$$\text{Proto-helium} \quad n = N'\left(\frac{1}{p^2} - \frac{1}{m^2}\right) \quad \begin{cases} p = 3 \text{ for "4686" series} \\ p = 4 \text{ for Pickering series} \end{cases}$$

If N' were exactly equal to $4N$, some of the lines of proto-helium would be coincident with those calculated by Rydberg for the Principal series ($p = 15$ in the first formula) and for the Sharp series of hydrogen ($p = 2$, $m = m + 05$ in the first formula) The observed values are $N = 109,675$, $N' = 438,879 \cdot 1 \pm 10$ (the latter from $\lambda\,4685 \cdot 98 \pm 001$), and Bohr has shown that their ratio is in very close agreement with his theoretical expressions for these terms when correction is made for the mass of the electron The above values of N and N' give a provisional value for the mass of the hydrogen atom in terms of that of the electron as 1836 ± 12, or 1855 ± 12 when the data are corrected to the International scale of wave-lengths.

The well-known line at 4686 which occurs in the solar chromosphere, and in some of the nebulæ, is undoubtedly the proto-helium line, and there are no indications in these spectra of another line at 4688 which would correspond with the calculated Principal line of hydrogen Until other evidence is forthcoming, it may be considered that the line spectrum of hydrogen consists only of the Balmer series and parallel series in the infra-red and Schumann regions.

In regard to more complex spectra, since N and $4N$ are constant, or nearly so, for the two classes of series, Bohr's theory suggests that arc series in general are produced by atoms from which only one electron has been removed by the exciting source, while spark series are produced when two electrons have been removed It has not yet been shown, however, how a single series of hydrogen or of proto-helium comes to be represented by a group of series in other spectra

The change in the character of the series in passing from arc to spark spectra suggests the possibility of further change in the same direction, leading to series which would require nine times the ordinary series constant in the formulæ representing them.   A preliminary examination of terrestrial and celestial spectra, however, has given no indications of the existence of such series

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The Emission of Electricity from various Substances at High Temperatures

By G W. C. KAYE, B.A., D Sc , and W F HIGGINS, B Sc.

(Communicated by R. T Glazebrook, F R S   Received May 1,—Read May 21, 1914)

(From the National Physical Laboratory)

INTRODUCTORY

In previous papers[*] an account was given of experiments in which ionisation currents of great magnitude were obtained from carbon at high temperatures   It was remarked that the largest currents appeared to be associated with the expulsion (at about 2000° C) of impurities, such as silica, alumina and iron, which are always present in commercial carbon. Such a result is perhaps not surprising in view of Wehnelt's[†] work on the alkaline earths and their large electronic emissivity when raised to a white heat, as for example in a Wehnelt cathode

Furthermore, Sir J J Thomson[‡] showed some years ago that oxides, when raised to a red heat in a crucible, gave out an excess of negative electricity, the most copious streams coming from the oxides of calcium and barium.[§] The currents generated were such as were readily indicated by an electroscope

The present experiments (which were carried out some months ago) were undertaken, in the first instance, to investigate the behaviour of the alkaline

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[*] Harker and Kaye, 'Roy Soc. Proc.,' A, vol 86, p. 379 (1912) ; A, vol 88, p. 522, (1913)   King (' Astrophys. Jour ,' Nov , 1913, p 330) has since repeated some of the experiments at Mount Wilson in connection with his work on "tube-arc" spectra.

[†] Wehnelt, 'Ann. d Phys.,' vol 14 (4), p 425 (1904), and 'Phil. Mag ,' July (1905). See also Jentzsch, 'Ann d Phys ,' vol 28, p 537 (1909)

[‡] J. J Thomson, 'Camb Phil Soc Proc.,' vol 14, p 105 (1906).

[§] Prof Thomson showed further that when various salts were heated, the sign of the resulting electrification was the same as that produced by friction of the dry salt when cold.

earths when raised to the very high temperatures attainable in a carbon resistance-furnace. The scope of the experiments was afterwards extended a little to include a number of other materials

At temperatures as high as those we have used, apparently all bodies emit considerable amounts of electricity, and graphite, the only convenient refractory substance available for constructional work at very high temperatures, shows the effect to a high degree.

We have therefore had to resort to a difference-method, the procedure adopted being to measure the electrical emission from a particular substance when it was heated in a graphite crucible, and then to repeat the experiment, under the same conditions, with the same or a similar crucible when empty. As the crucible, in some cases, absorbed the fused material and thus became permanently contaminated, the reverse order was, as a rule, the more convenient. For each material tested, a new crucible was substituted.

The temperatures employed ranged from about 2000° to 2500° C —high enough, in every case, to volatilise rapidly the substance under test.

In all the experiments, two independent circuits were utilised to measure the ionisation. In one of these, the ionisation current was measured between the crucible containing the evaporating substance and the furnace wall.

For the other circuit, an additional carbon electrode was permanently mounted in the furnace (see fig 1). The carbon electrode was hollow and
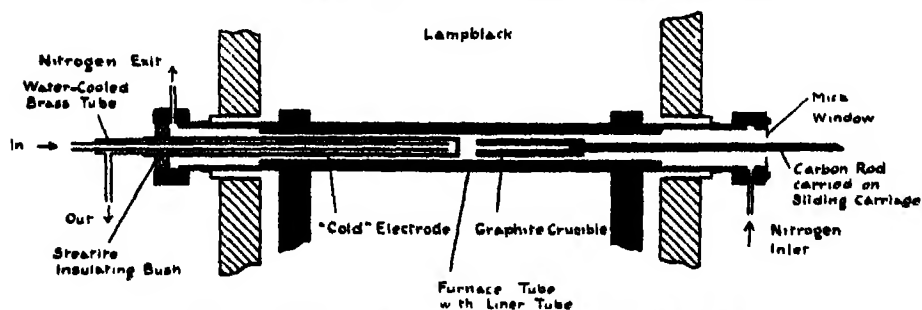

Fig 1.—Showing carbon-tube furnace and electrodes.

contained an inner brass tube cooled by a rapid stream of water. There was thus a considerable difference of temperature between the electrode and the furnace-tube, and this temperature-difference evidenced itself in the form of a steady ionisation current across the atmosphere of the furnace, the current-measurer being joined to the furnace-tube and electrode. The object of the cooled electrode was to see if the introduction of the substance under test affected the degree of ionisation in the furnace atmosphere; whereas any effect due to evaporation of the material or to chemical reactions in the crucible would naturally be recorded in the circuit containing the crucible.

In no case was any electromotive force applied   the currents recorded were entirely unaided other than by the conditions in the furnace   Nor are the effects due to any kind of rectification or leakage from the alternating current
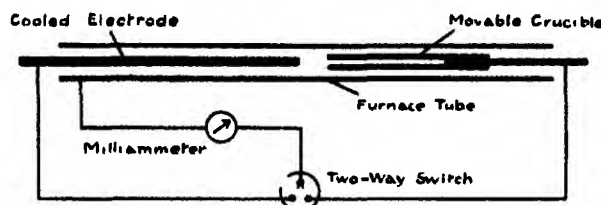

Fig 2 —Electrical connections

used to heat the furnace   the phenomena persisted, if to a somewhat less extent, when the heating current was momentarily shut off

APPARATUS

The general arrangements are shown in fig 1   The carbon furnace-tube was about 75 cm long, of which a central portion, about 36 cm long, was subjected to the heating current   The internal diameter of the tube was 30 mm and the thickness of wall 4 mm

A number of the materials tested were found to react with the furnace-tube, with results disastrous to its longevity   To obviate the nuisance of repeatedly mounting a new furnace-tube, the plan was adopted, in the later experiments, of inserting a thin carbon tube as an inner lining to the furnace   This liner-tube was renewed from time to time as occasion required

The ends of the furnace-tube were closed with graphite caps, through the sides of which passed small tubes providing ingress and egress for a stream of nitrogen gas   The nitrogen served to check the oxidation of the carbon tube, while the current of gas prevented the formation of condensed " cobwebs " of material across the furnace-tube, to the detriment of measurements of both ionisation and temperature

The crucible consisted of a short length of graphite tube (about $5\frac{1}{2}$ mm internal diameter) mounted horizontally at the end of a carbon rod, the open end of the crucible pointing towards the cold electrode, as shown in fig. 1. The carbon rod was supported on a sliding carriage, and the crucible passed in and out of the furnace through a hole in a mica window

RESULTS

Among the substances tested were the alkaline earths (BaO, CaO, SrO, MgO), soda-lime, alumina (Al_2O_3), oxide of iron (Fe_2O_3), silica (sand), and the metals, tin, copper, aluminium, iron, and brass   Usually the substance

was in a state of powder. In most instances, the effect of suddenly introducing the various substances into the hot furnace was a little violent A puff of smoke or flame occasionally shot from the furnace mouth, evidence of violent boiling being plainly recognisable in some cases The absorption of the white light from the incandescent central region of the furnace by the vapour in the cooler parts of the tube imparted, in some instances, a striking coloration to the emitted light Some of these colours were obviously complementary in tint to those usually associated with thermal excitation. For instance, CaO gave a yellow-green colour, BaO a beautiful salmon-pink, and SrO an intense green, aluminium gave a brilliant yellow, and Al_2O_3 a beautiful green

With one exception, all the substances behaved like carbon and emitted copious streams of negative electricity at the high temperatures employed.

Oxides

Baryta, BaO —At each introduction of the baryta the "crucible-current" increased temporarily six or eight fold, attaining 1 ampère in one instance. The increase remained to some extent on a second heating, and this is accounted for by the expulsion of the salt which had been absorbed by the graphite crucible The "electrode-current," which was at first somewhat diminished by the BaO, afterwards considerably increased This increase persisted even when an empty crucible was substituted, doubtless owing to the continued activity of the residual atmosphere produced by the BaO

Lime, CaO —In the case of lime the crucible-current showed, instead of a rapid growth, a steady increase (up to $\frac{1}{4}$ ampère) with each successive heating of the crucible One would infer that some of the lime was absorbed by the carbon and that the proportions of the reacting substances became more favourable as the heating progressed This peculiarity was not confined to the lime, most of the materials showed it on occasion

Soda-lime —Soda-lime was also tried to see if the presence of the soda would enhance the effect of the lime No certain effect could be detected, probably owing to the too rapid volatilisation of the soda

Strontia, SrO —In one experiment, strontia, introduced as $Sr(NO_3)_2$, doubled the normal ionisation current at a temperature of 2000° C

Magnesia, MgO —Magnesia behaved very like lime and baryta The crucible-current increased temporarily six or seven fold (to 750 milliampères), while the electrode-current at first diminished a little and then greatly increased

Silica, SiO_2.—Silver sand was employed. The crucible-current rose from about 360 milliampères to 580 milliampères, the electrode-current meanwhile

increasing slightly from about 120 milliampères to 145   The temperature was about 2400° C

Alumina, Al_2O_3 —The crucible-current increased to over an ampère, i.e., from 10 to 20 fold, when the alumina was introduced   The addition of more alumina after a few heatings produced no further increase—the furnace-atmosphere was, so to speak, "saturated"   The electrode-current exhibited a considerable and permanent increase

Oxide of Iron, Fe_2O_3 —The introduction of Fe_2O_3 doubled the crucible-current   The reduced iron attacked the furnace-tube vigorously and the run soon terminated

Metals

With a view to simplifying somewhat the chemical conditions, the effect of introducing a few metals into the furnace was investigated

Tin.—When tin was introduced the crucible-current was increased 10 times (to 600 milliampères), but the electrode-current showed only a small increase

The increase in the crucible-current completely disappeared after a first heating   This is explained by the fact that under the conditions which prevailed, the tin was probably not subjected to any chemical attack, but was wholly expelled from the crucible by boiling.

Aluminium —When aluminium was introduced both crucible-current and electrode-current were increased from about 120 milliampères to a maximum of about seven fold   Unlike the emission from tin, the effect persisted and even increased on subsequent heatings   We should explain this as due to the retention of some of the aluminium by the carbon (possibly as carbide), and its gradual expulsion, on further heating

Iron —The introduction of iron in the crucible trebled the crucible-current (from 160 to 460 milliampères), and raised the electrode-current about 50 per cent   It is worthy of note that if we extrapolate to 2500° C the emissivity-temperature curve of iron obtained by Harker and Kaye (*loc. cit.*) for temperatures up to the melting point (1500° C), we derive a current of the right order, but somewhat smaller than that now found   The iron behaved like its oxide in attacking the furnace-tube

Copper.—The crucible-current was increased four fold (to 220 mgrm), the electrode-current only slightly.   Just as with tin, the effect almost disappeared on a second heating.

Brass —Brass provided the one exception to the otherwise complete unanimity with which all the substances emitted negative electricity.   On its first heating the brass gave out, as a rule, a large quantity of positive electricity   In one case the boiling brass generated a positive current amounting to no less than 140 milliampères

DISCUSSION.

It will be apparent, from a scrutiny of the foregoing results, that there is in every instance a large evolution of electricity when a substance is suddenly vaporised in the furnace   From the work carried out by Richardson, Pring, and others, together with the previous experiments conducted at the National Physical Laboratory, it would appear that we may look to at least three sources for the electricity generated by a rise of temperature —

(1) The electronic emission, which is a function purely of the temperature,

(2) That due to chemical reactions, and probably

(3) That produced by a change of state—vaporisation, and possibly liquefaction.

The conditions in the present experiments are so complicated that we could scarcely hope to explain the results from any single standpoint   Doubtless all three causes are operating, the second and third being the more important It does not follow, of course, that all three effects would be of the same sign

In regard to the effect of chemical activity, we have to bear in mind that, together with the test-material, there are always present carbon and nitrogen   High-temperature chemistry is both difficult and obscure, and at present we do not know what are the probable reactions (if any) with some substances   We do know, however, in the case of the alkaline earths, that both lime and baryta form carbides with carbon, such carbides being more fusible and more volatile than the original oxides. At very high temperatures, carbonyls, cyanides, etc, probably also act as intermediaries, followed by complete dissociation

We are aware, too, that a curious reaction occurs between solid magnesia and carbon at about 1900° C, the magnesia merging into the carbon in a manner strongly suggestive of fusion, the melt being, however, quite a spurious one, the true melting point being some 300° higher. Then, again, iron and carbon at high temperatures have a powerful affinity for each other, for example, molten iron rapidly eats its way through a graphite crucible owing to the formation of a low melting-point carbide. We might expect a carbide reaction to operate also in the cases of silica and alumina.

But, so far as we know, tin and carbon do not react, and neither do copper and carbon, and so in these cases the large emission may be due wholly to causes (1) and (3). In the case of the brass, it may be that the vaporisation effect is positive in sign, the electrification produced being sufficiently in excess to mask completely the negative emission due to temperature.

Possibly the low boiling point of the zinc is responsible for the positive emission

In considering the intensity of the ionisation currents obtained, we may note that the open end of the crucible had an area of about $\frac{1}{4}$ sq cm   If it is legitimate to assume that this was the effective area of evaporation of the volatilised materials, it follows that the ionisation currents attained in some cases an intensity of 4 ampères per square centimetre, which may be regarded as a generous estimate

In conclusion, we may be allowed to touch briefly on the question (previously referred to by Harker,[*] on the basis of some earlier experiments) of the applicability of the present results to some of the problems of solar electricity   Many of the substances with which we have experimented, *eg*, Ca, Mg, Fe, Al, occur in great abundance in the sun, and hitherto no quantitative data as to their electrical behaviour at very high temperatures has been available   As is now well known, Hale concludes from his spectio-heliographic researches that a sunspot is the region at which a solar vortex emerges at the surface   Without a doubt, the matter transported by such a vortex from one part of the sun to another would experience enormous variations in temperature, and we can therefore conceive how, as a result, the whirlpool in a sunspot is largely made up of electrified particles

In the present experiments we have obtained current-densities of the order of 4 ampères per square centimetre at 2500°   Now, the rate of increase of the electrical emissivity with temperature is very rapid, and, if extreme extrapolation of measurements obtained over the range of temperatures possible in a tube-furnace may be regarded as legitimate, it would appear that at the estimated temperature of the sun, say 6000° C , such a current-density would be increased millions of times.

Thus, notwithstanding the gigantic areas of sunspots,[†] there is no difficulty in accounting for the enormous currents necessary to produce the magnetic fields (some 2000–5000 gauss), which Hale has shown to be associated with sunspots.   On the same lines we may seek to explain also the sun's general magnetism, the vertical component of which at the poles Hale has estimated at about 50 gauss

SUMMARY.

Experiments have been conducted at temperatures fram 2000 to 2500° C. within a carbon-tube furnace at atmospheric pressure.   Under these

[*] Harker, 'Monthly Notices, R.A.S ,' June, 1913, p 562.

[†] The average diameter of what may be regarded as a spot of normal size is from 10,000 to 20,000 kilom , though much larger spots have been observed.

conditions the electrical emissions, in the absence of any applied potential, have been measured for a number of substances (including the alkaline earths and the metals tin, aluminium, iron, and copper) on their introduction into the furnace. During their rapid volatilisation the substances gave out large amounts of electricity, which, with one exception, was negative in sign. For example, barium oxide and alumina generated negative currents of the order of 4 ampères per square centimetre, boiling tin about 2 ampères per square centimetre, and boiling iron about 1 ampère per square centimetre Boiling brass, on the contrary, produced a positive current of about 0 5 ampère per square centimetre The results have interest in connection with the problems of solar magnetism

Incidentally, striking absorption-colorations were obtained when the light from the furnace was transmitted through the vapours of the alkaline earths, *e g*, the emergent light in the case of strontia was coloured a brilliant green, and with baryta a salmon-pink

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An Application of Electrolytically Produced Luminosity, Forming a Step towards Telectroscopy

By L H WALTER, M A

It has long been known that in valve cells the anode becomes luminous when the potential difference across the cell exceeds a certain value, and Šebor and Šimek* have shown that the luminous property is enhanced when the anode is not of pure aluminium

The first to make practical use of this property appears to have been G. J. Johnstone,† who found that an aluminium alloy containing as much as 10 per cent of some metal which exhibits no valve effect *per se* (*e.g*, copper, tin, etc.) gave a greatly improved luminous effect, in fact, according to his claims, one of quite a different order.

About three years ago the author determined to repeat Johnstone's experiments with a view to seeing if the idea could not be applied to certain purposes which the author had in view.

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* 'Zeitschrift für Elektrochemie,' vol. 13, p. 113 (1907).
† 'Electrical World,' vol. 52, p 343 (1908).

With a cast alloy as described by Johnstone a certain luminous effect was noticed but cast metal was not suitable for the author's purpose   With rolled or drawn alloy it was found in general that corrosion rapidly set in, leading ultimately to reduced voltage across the cell and extinction of the luminosity : until this corrosion became very marked, however, it only had the effect of increasing the leakage current.   On trying a number of alloys it was observed that duralumin—an aluminium alloy commercially obtainable in the rolled and drawn forms—gave a very much greater luminous effect than Johnstone's alloy at the same voltage   Corrosion took place, however, just as rapidly as with the other alloys, and the remarkable feature was that the more usual electrolytes which give good results with pure aluminium showed up very badly when duralumin was used, ammonium borate, particularly, causing bad corrosion

After a prolonged series of trials two electrolytes, namely sodium tungstate and sodium molybdate, were found which, while giving a satisfactory valve effect, showed practically no tendency to attack the duralumin under ordinary conditions, although both electrolytes quickly corroded other aluminium alloys containing zinc or tin   This gave the clue to the favourable behaviour of duralumin, which contains neither of the two latter metals but only about $3\frac{1}{2}$ to $5\frac{1}{2}$ per cent of copper, $\frac{1}{2}$ per cent of magnesium, and a small amount of manganese.

Having now at his disposal a suitable alloy and electrolyte the author was able to proceed towards the attainment of his object, and succeeded in constructing various luminous devices, out of sheet alloy or wire, which enabled rapid changes of design to be exhibited   These devices were immersed in a glass tank containing the electrolyte, and were viewed through the glass of the tank   This arrangement presents no special features of physical interest and so will be passed over

In the course of the experiments it was found that the glass front of the tank became dimmed and coated with a deposit from the electrolyte when the device had been working or even standing for some time · further, the submerging of the metal and the carrying up of the necessary contact wires so that they should emerge from the electrolyte in a suitably insulated condition presented difficulties   It was, therefore, sought to dispense with the tank and to arrange that the liquid should flow down the face of the alloy   As a matter of fact the capillary effect of the film was found to act so effectively in keeping the surface wetted, that if the bottom edge of a sheet of alloy was dipped into the electrolyte and held there, the moisture retained would suffice for the luminous effect to be obtained, but only for a short time owing to the heating.   Still, the behaviour of the alloy under these conditions suggested

that it would be possible by assisting this surface action to turn it to practical use, provided a sufficiently transparent material could be applied to the surface to act as a means of spreading the electrolyte over it.

It was finally found that a sufficient and equally distributed layer of liquid flowing down the face of the alloy to be rendered luminous could be secured by the simple expedient of hanging a wetted piece of crêpe de Chine in front of the alloy, in such a way that it clings to the face of the metal, and letting the liquid flow down over the surface, the circulation of the liquid being secured by means of a small centrifugal pump driven directly by a small electric motor

The successful solution of the problem of how to dispense with the glass tank had a rather interesting result

It of course became obvious that, since the luminous member no longer had to be immersed the conducting leads could be passed out at the back of the luminous object, which latter was generally supported on an ebonite or other insulating sheet, and since at the back of the sheet there is no liquid flowing and the metal is dry there, the whole arrangement of contacts could be got at conveniently

This at once suggested that,.by making up the luminous anode out of a very large number of equal units, wetted in front and supplied with current at the rear, a long-sought-for arrangement could be arrived at, namely, a simple and inexpensive apparatus comprising a vast number of separately contiollable equal units which can be made luminous in any grouping or sequence desired, in brief, such an apparatus as has often been pictured mentally as a visual receiver in the case of phototelegraphy and even telectroscopy

In the author's crude experimental apparatus he has been able to obtain 5,500 separately control-lable luminous units in a space little larger than the size of a cabinet photograph, equivalent to more than 24,000 per square foot.

The way in which the electrical connections are made is shown in the figure. This gives, on an enlarged scale, a sectional end elevation of a small part of the anode, comprising the alloy units or studs s, s, and their supporting sheet of ebonite e.

The electrolyte escapes from holes h in the pipe p and flows down the faces of the studs, the flow being distributed by the crêpe curtain c, which is supported from the pipe p.

The most suitable voltage to work at is from 130 to 140 volts, the negative
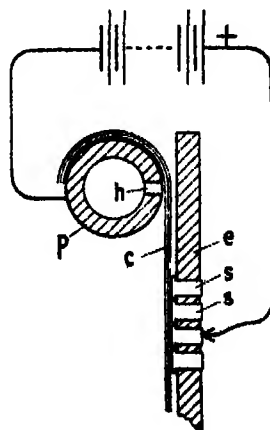
terminal of a direct current electric supply being connected to p, while the positive lead makes contact with the backs of those studs which it is desired to make luminous

The arrangement can be used for quite a number of purposes, and it is proposed to publish later the results of experiments in the reproduction of photographs, etc For the present, in this preliminary paper, it is merely desired to point out that a new means is now available, by which, within a small compass, an almost unlimited number of separately controllable luminous areas can be obtained , that such areas or points, can have their luminosity graded, by means of the applied voltage , that such luminosity can be established, or extinguished, at least some hundreds of times per second , and that, since all the luminous points are automatically in parallel, being all connected to the negative pole (the electrolyte), only one contact is needed for each alloy unit

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The Axial Chromatic Aberration of the Human Eye.

By P G Nutting

A bright object viewed directly by a normal human eye shows no perceptible coloured fringes. From this it has been assumed by some that the eye is fairly well corrected chromatically, at least for the most luminous constituents of white light On the other hand, if the same object be viewed through a filter transmitting only the extreme red and blue, it will appear with either a red or blue fringe, showing that for these extreme rays the eye is not corrected.

Helmholtz[*] passed monochromatic light through a small hole and found that when red light was used, the hole appeared in best focus when viewed from a distance of about 8 feet With blue illumination it appeared brightest at about $1\frac{1}{4}$ feet, and with extreme violet but a few inches (nur einige Zolle) With these rough determinations of Helmholtz the question appears to have rested

With the aid of very simple apparatus it was found possible to obtain rather precise determinations of axial focal length The test object used was the

[*] ' Physiolog. Optik,' 3rd edit , 1909, vol. 1, p. 147.

image of the slit of a monochromatic illuminator (S, fig 1) formed by a movable lens L of about 20 cm. focal length   At a fixed distance (about 20 cm) back of this was the observer's eye, E.   In order to fix the accommodation, there was placed immediately in front of the eye a plate of optical glass, P, reflecting the image of a suitable object at the desired distance

Three eyes were tested at accommodations of 25 cm, 100 cm, and ∞ , tho remainder at ∞ only   The object serving to fix the accommodation was so chosen that the slit image appeared against a dark background such as a distant tree trunk or a black printed letter, so that a barely perceptible amount of white light was mixed with that of the coloured slit image   In making determinations at wavelengths 406 and 436 a mercury arc was used as source, at other wave-lengths a Nernst lamp   A shift of the lens 1 cm corresponded to 0 01 mm shift in focal point at the retina, the relation between the two being roughly linear   The uncertainty on a group of five settings was not over 2 mm , results could be reproduced at different times to about 5 mm on the scale

All the subjects chosen had good normal vision.   Two, C. H B and C E S, were women   Four, L. A. J., P G N, C. E S, and M B H, were experienced in photometric observations, the others, practically without experience in such work L. E J has marked natural ability, and has had long experience in colour work

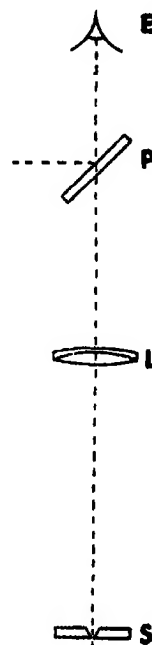The results obtained are given in the following tables and in fig 2   Data

Accommodation ∞

Wave-length	Subjects						
	L A J	P G N	L E J.	C E S	C H B	M B H	J D H
780	0 010	0 013	0 004	0 020	0 006	0 016	0 012
740	0 009	0 010	0 011	0 017	0 004	0 010	0 011
700	0 002	0 005	0 009	0 007	0 003	0 008	0 008
650	0 000	0 000	0 005	0 003	0 002	0 004	0 008
600	0 000	0 000	0 000	0 001	0 001	0 000	0 001
550	−0 003	0 000	−0 005	−0 001	−0 001	−0 004	−0 004
550	0 003	0 000	0 005	0 001	0 001	0 004	0 004
500	0 014	−0 006	0 012	0 005	0 005	0 014	0 011
465	0 025	0 020	0 022	0 024	0 012	0 022	0 024
436	0 036	0 039	0 038	0 031	0 022	0 031	0 032
406	0 051	0 064	0 050	0 042	0 038	0 048	0 052

Fig 1

| Wave-length	L A.J			P G N			J D H		
	∞	100 cm	25 cm	∞	100 cm	25 cm	∞.	100 cm	25 cm
780	0 010	0 011	0 014	0 013	0 014	0 020	0 012	0 011	0 016
740	0 009	0 010	0 010	0 010	0 012	0 016	0 011	0 012	0 018
700	0 002	0 003	0 003	0 005	0 004	0 009	0 006	0 006	0 011
650	0 000	0 000	0 001	0 000	0 001	0 004	0 003	0 005	0 007
600	0 000	0 000	0 000	0 000	0 000	0 000	0 001	0 001	0 001
550	−0 003	−0 002	−0 004	0 000	−0 002	−0 005	−0 004	−0 005	−0 005
500	0 014	0 011	0 019	−0 006	0 005	0 011	0 011	0 013	
465	0 025	0 023		0 020	0 012		0 024	0 022	
436	0 036	0 038		0 039	0 032		0 032	0 038	
406	0 051	0 049		0 064	0 054		0 052	0 054	
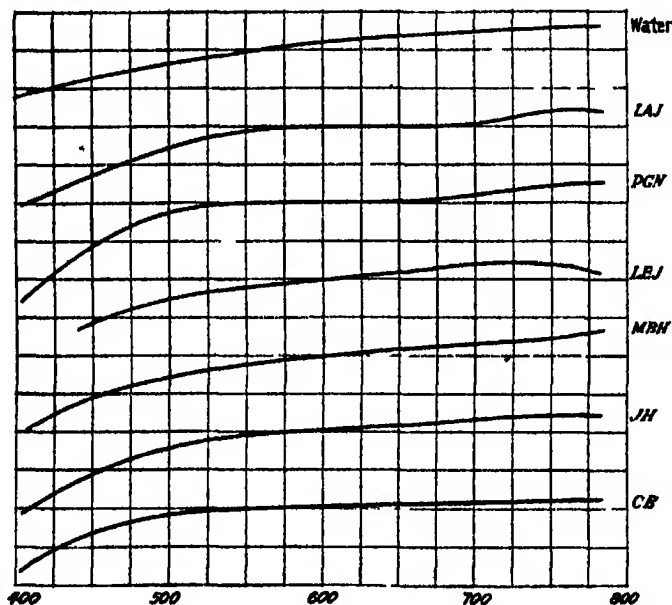
Fig 2

are given as relative focal differences, $\delta v/v$. From these, approximate distances in millimetres of focal points from the retina may be obtained by multiplying by 15

All the eyes tested show more or less correction For comparison, the axial error of an eye of pure water is given at the top of the figure In the most luminous part of the spectrum, from 520 to 660, all eyes show less variation in focal length than an equivalent eye of pure water would have In some eyes the correction in the central region would compare favourably with that of a good photographic or telescopic objective.

Several types of correction are shown that are new to lens optics

The high order central corrections of L. A. J and P G N. are accompanied by decreased violet but normal red correction   L E J. shows no correction except in the extreme red and violet, where the correction is normal   M B H. is slightly corrected except in the extreme regions   C H B is fairly well corrected over a wide region from 480 to 780

Tests were made for residual chromatic spherical aberration (departure from Gauss condition) by placing half of a half-tone screen over the test slit   The writer could detect no residual in his own eye in the region from 500 to 650 Beyond 700 in the red and beyond 480 in the blue it is noticeable, while at 406 in the violet it amounted to fully 20 times the normal diffusion.   L A J agreed with the writer but L E J could detect little loss of definition at 406

I wish to record my indebtedness to Mr Eastman and Dr Mees for apparatus and to those of my assistants who served as subjects

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On Anomalous Trichromatic Colour Vision

By W. WATSON, D.Sc, F R S

Having occasion to examine a large number of persons who have abnormal colour vision, the author has found that the so-called anomalous trichromates are clearly divisible into two groups, which groups can be sharply differentiated by quite simple experimental means   By anomalous trichromate is meant a person who, while not a dichromate, i.e, a person who can match all colours of the spectrum by a mixture of two suitably chosen monochromatic lights, has not got normal colour vision   Such cases were first investigated by Lord Rayleigh, and have since been investigated by many observers. It has already been noticed by several investigators that there are two classes of anomalous trichromates   These are distinguished by the fact that when a monochromatic orange (D-light) is matched by a mixture of green and red light one class, the protanopes, take more red in the mixture than the normal, while the other class, the deuteranopes, take more green than the normal. The following paper is intended to prove that both of these classes require to be subdivided, or rather that anomalous trichromates ought preferably to be divided into two other classes, and then each of these classes subdivided into protanopes and deuteranopes.

As has been pointed out by Sir W. Abney, if white light is transmitted through a thickness of about 0 8 cm of a saturated solution of chromate of potash the colour of the resulting light can be matched by a single spectral colour, and, further, in the case of persons having abnormal colour vision the wave-length of the spectral colour differs from the one which matches the chromate light for the normal   As a result of applying this test to a large number of persons who have not got normal colour vision, the author noticed that, while for some observers the monochromatic colour which matches the chromate light is of quite definite wave-length, for others a band of the spectrum matches the chromate light, further, that one edge of this band always coincides with the position which matches the chromate light to the normal eye   Thus if a slit is traversed through the spectrum and the light which passes is received on a screen alongside the light which has traversed the chromate solution and the position noted when the two lights match, the slit being moved alternately first from the red end of the spectrum and then from the green end, in the case of persons having normal colour vision the settings will he between 578 and 580 $\mu\mu$ when the source of the white light is the electric arc   With one class of abnormals, which will be called class A, the setting coming in one direction will agree with the normal setting, but the setting coming in the other direction will differ markedly from the normal setting   This class is divided into two subdivisions, one, A_r, in which the abnormal setting, and hence the whole of the band of the spectrum which matches the chromate light, lies on the green side of the normal match, and the other, A_g, where the band lies entirely on the red side of the normal   It must be remembered that the match with the chromate appears to be equally good throughout the band included between the extreme settings, and, further, that one edge of the band always coincides with the normal setting.

In the case of the other group of abnormal trichromates, which will be called class B, the match with the chromate light differs from the normal, but whichever way we move the slit the position for which the match is satisfactory is the same   Of course individual settings differ slightly, but the differences are no greater than those obtained when a normal makes the settings.   Up to now all the members of this class which have been met with obtain a setting which lies on the red side of the normal setting.   If, however, further investigation should bring to light persons who obtain a definite point of setting which lies to the green side of the normal, then this class would have to be subdivided as is class A

Another method of distinguishing the two classes is to match white by means of a mixture of violet (400 $\mu\mu$) and yellow, that is to determine the

complementary to the violet   Thus if a slit is moved through the spectrum in the neighbourhood of the yellow and the light is mixed in suitable proportions with violet light which passes through a second slit a match with white can be obtained, and the procedure adopted when making a test is exactly the same as with the chromate light   In the case of the normal the position of the yellow slit will vary between 574 and 577 $\mu\mu$, the white being the light from an electric arc   With class A the setting for the yellow slit when approaching in one direction always agrees with the normal, but the setting obtained when approaching in the other direction differs markedly from the normal setting, for a position of the slit anywhere between these two limits the match appearing equally good   This region again is always bounded on one side by the position of the normal setting, but while for members of class A_r it stretches towards the green, for members of class A_g it stretches towards the red

Persons belonging to class B have a complementary to violet which differs from the normal to various extents, but they differ from class A in that whichever direction we move the slit when making the match the position of setting is the same, the accuracy with which this position is located in the spectrum being, if anything, greater than that with which the corresponding setting can be made by normal observers

The Table on p 446 gives the results of the examination by these two methods of a number of persons who all possessed abnormal colour vision   In each case two settings were made with the slit moving in each direction, and in the table are given the means of each pair of settings, *i.e*, the mean of the two settings when the slit was moved up the spectrum, and the mean of the two settings obtained when the slit was moved down the spectrum.   In the table the results have been subdivided according to the classification given above, but in each class they are arranged in chronological order.   When examining the numbers it must be remembered that in every case the observer was quite unused .to making colour matches or any other measurements of the kind.   The slit was in every case moved at a fairly uniform rate by the author, and the observer was asked to say "Stop" when the two patches of light, which were alongside one another, appeared to him to be of exactly the same colour.

On the Young-Helmholtz trichromatic theory we can explain the classification given above   Thus all members of class A are persons with defective red or green sensation.   In the case of A_r the red sensation is defective, and this class would include as an extreme case that where the red sensation is completely absent, that is a protanopic dichromate, while at the other extreme we should have the normal   The examples given in the Table are

Match with chromate light	Complementary to violet (400 μμ)

CLASS A

Sub-division A_r

Match with chromate light	Complementary to violet (400 μμ)
562 to 578 μμ	
554 „ 578	567 to 576 μμ
560 „ 577	540 „ 574
570 „ 580	566 „ 577
571 „ 582	557 „ 576
562 „ 580	568 „ 575

Sub-division A_g

Match with chromate light	Complementary to violet (400 μμ)
576 to 598 μμ	575 to 590 μμ
579 „ 586	
578 „ 592	
574 „ 591	
580 „ 599	574 „ 590
582 „ 592	578 „ 586
581 „ 591	576 „ 581
579 „ 590	577 „ 585
579 „ 591	576 „ 586
580 „ 598	575 „ 588
575 „ 598	572 „ 583
581 „ 594	575 „ 585
580 „ 590	577 „ 590
579 „ 595	579 „ 588
579 „ 598	575 „ 592
579 „ 591	575 „ 587
578 „ 597	575 „ 595

CLASS B

Match with chromate light	Complementary to violet (400 μμ)
594 to 594 μμ	594 to 596 μμ
590 „ 595	591 „ 593
590 „ 591	590 „ 590
587 „ 591	586 „ 587
586 „ 589	581 „ 584
587 „ 588	587 „ 587
590 „ 591	590 „ 591
586 „ 591	582 „ 585
588 „ 589	583 „ 589
587 „ 591	588 „ 587
588 „ 588	579 „ 582
584 „ 590	587 „ 589
585 „ 587	584 „ 584
587 „ 589	588 „ 589
589 „ 593	587 „ 588
586 „ 586	584 „ 587
586 „ 587	585 „ 587
587 „ 588	584 „ 584

all cases where the red sensation is very much in defect, that is they approach the dichromate condition. The luminosity curves of all these observers are such as would be obtained if the red sensation was defective, and agree with the calculated curves given in a previous communication to the Society.[*]

[*] 'Roy. Soc. Proc.,' A, vol 88, p. 404 (1918).

The members of the division A_g have in the same way a defect in the green sensation In this case the amount of the defect varies greatly, though the greater proportion seem to have a green sensation which amounts to about half the normal Here again the luminosity values agree with those calculated on the assumption that the green sensation is defective *

Members of class B are such that the red-sensation curve is exactly the same as the normal The green sensation is as strongly developed as in the normal, but the green-sensation curve appears to be displaced towards the red end of the spectrum, the displacement varying to a certain extent in the case of the different persons The result of this displacement is that the point in the spectrum where the red- and green-sensation curves intersect is displaced towards the red Hence the complementary to the violet is displaced to an equal extent A typical case of such a displaced green-sensation curve has been described in detail in a paper by Sir W Abney and the author *

If the Rayleigh match of spectral orange with a mixture of green and red is used to test these anomalous trichromates, it will be found that while members of class B make a very definite match, which differs from the normal in that it contains much more green, yet the accuracy with which they make the match is as great as in the case of persons having normal vision On the other hand, members of class A often make matches which differ from the normal, but yet their successive settings will differ considerably, and will, in general, approach the normal setting as one limit. This test is not, however, nearly as convenient as those described in this paper, owing to the fact that the orange produced by mixing green and red is less saturated than the spectral orange, and different observers, or even the same observer at different times, seem very uncertain as to the allowance to be made on account of this want of saturation

Although the settings obtained by members of class B in the two tests described above are satisfactorily explained by a displacement of the green-sensation curve, the explanation of the settings obtained by members of class A is not so obvious It is fairly evident that in the case of class A we have to do with a reduction form of normal colour vision, so that in A_r the red sensation, and in A_g the green sensation, is less well developed than in the normal. Because in the case of such reduction forms we should expect a want of definiteness in making the colour matches. Hence the fact that in class A a considerable band of the spectrum is matched with the chromate light or can be combined with a given violet to form white supports the view that this class is a reduction form, yet it does not explain the position

* 'Roy. Soc. Proc.,' A, vol. 89, p. 232 (1913).

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of this band. For the band does not extend on both sides of the position corresponding to the normal setting, but lies entirely on one side At present the author is not in a position to offer any explanation of this fact. The distinction between classes A and B appears to him, however, of such fundamental importance, when considering the connection between heredity and colour blindness and also when studying the incidence of this condition in different peoples, that he has decided to publish the results he has obtained up to now without waiting till, by further experiments, more light has been thrown on this particular difficulty

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Note on Mr. Mallock's Observations on Intermittent Vision.

By SILVANUS P. THOMPSON, F.R.S

In the paper communicated by Mr Mallock on December 11, 1913,[*] in order to account for the intermittences seen when watching a revolving disc of black and white sectors, at the moment when a slight mechanical shock is given to the head or body, he advances the hypothesis that a slight mechanical shock of any kind produces a periodic but rapidly extinguished paralysis of the perception of light, and that the nerves on which seeing depends cannot bear more than a certain amount of mechanical acceleration without loss of sensibility

This hypothesis of a momentary paralysis of the sense of vision seems unnecessary   The sector disc revolving at from two to six revolutions per second presents a uniform grey tint   At the moment when the intermittence occurs, by stamping the foot or tapping the head, the most prominent effect observed by the writer was not the momentary appearance of stationary grey or black sectors, but the enhanced brightness of stationary white sectors.   A momentary paralysis, if it occurred, should produce momentary blackness of the entire disc, which is not what happens.

To put the phenomenon to further test, a revolving sector disc, driven uniformly by a small electric motor, was arranged so that it could be observed either directly from a distance of a few feet or by reflection in a small sheet of mirror-glass held in the hand or clamped elastically between two india-

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[*] 'Roy. Soc. Proc.,' A, vol. 89, p. 407.

rubber corks upon a solid support. When a slight mechanical shock is given to the mirror so as to alter momentarily by a small amount the apparent position of the revolving disc, an intermittence is produced of the same kind as is observed when a shock is given to the head or body. The sectors appear momentarily to stand still, and the brightness of the white sectors is for an instant enhanced. This intermittence, if such it can be called, occurs equally whether the observer taps the mirror or whether some other person taps it. The phenomenon is in this case independent of any mechanical acceleration of the nerves or nerve-structures, and is not due to any temporary paralysis of vision. Though shocks of different force and duration produce slightly differing appearances, the writer can observe no difference in kind between the effects of shock to his own head or body and those of shock given to the mirror. Nor does he find any difference between the effects of shocks made by his own muscular effort and those of shocks made by other persons when he is watching the image in the mirror

The explanation appears to be that when the moving images of the white sectors on the retina are suddenly shifted by a minute displacement, they fall on some of the rods and cones which are relatively unfatigued, and which, for the instant, are therefore of greater sensitiveness.

The Variation of Electrical Potential across a Semi-permeable Membrane *

By Prof F. G Donnan, F R.S , and G M Green, M Sc

Introduction.

It was shown by Donnan† that in certain cases the potential difference between two solutions of an electrolyte, separated by a membrane which is impermeable to the electrolyte, but permeable to the solvent, can be calculated. Thus, suppose the solutions (1) and (2)

$$
\begin{array}{ccc}
 & \mathbf{K} & \mathbf{K} \\
(1) & \mathbf{A}' \quad\Big|\Big| \quad \mathbf{A}' & (2) \\
 & c_1, \ \pi_1 \qquad c_2, \ \pi_2 &
\end{array}
$$

of the electrolyte KA are separated by a membrane which does not permit the salt KA to pass, though freely permeable to other salts, with, say, the same cation K. We may then ascribe the potential difference set up at the membrane as due to the tendency of the K ions to equalise their concentrations. If we assume the permeable ions to obey the laws of ideal solutions, then

$$\pi_2 - \pi_1 = \frac{RT}{nF} \log \frac{c_1}{c_2},\qquad(1)$$

where c_1, c_2, are the molar concentrations of the K ions, n their valency, R the gas constant, F the quantity of electricity associated with a gramme-equivalent of ionic matter, and π_1, π_2, positive potentials of the solutions. For univalent ions and 18° this reduces to $\pi_2 - \pi_1 = 0\,058 \log (c_1/c_2)$ volts. If the permeable ions cannot be assumed to follow the laws of ideal solutions, we must substitute for c_1 and c_2 the quantities termed by G. N. Lewis‡ the "activities," or else (as is readily done) obtain an equivalent equation, involving, instead of c_1 and c_2, the ordinary thermodynamic potentials of the ions. In the following paper an account is given of an attempt to test equation (1) by measurements of the potential difference between two aqueous solutions of potassium ferrocyanide, separated by a membrane of colloidal copper ferrocyanide.

Experimental Arrangements.

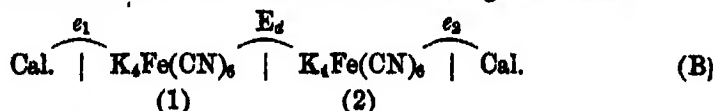The membranes of copper ferrocyanide were made in the following way An aqueous solution of copper sulphate of 3-per-cent strength was separated in a suitable manner by good vegetable parchment from a 7-per-cent aqueous solution of potassium ferrocyanide * After three days the parchment membrane was removed, washed, and then placed in contact with the same solutions, but in reverse order, for another three days Finally, it was taken out, well washed, and preserved under water. Parchment membranes prepared in this way proved to be quite impermeable to potassium ferro-cyanide of the concentrations used in the present work.† It is necessary, however, to preserve them under water, as they gradually lose their impermeability on drying Discs were cut from the prepared parchment and firmly fastened to glass tubes, the ends of which had been turned over to a wide and smoothly ground flat flange The joint was made tight by Golaz cement and paraffin wax. The membrane vessel so constructed contained one of the solutions of potassium ferrocyanide and dipped into the other solution. Syphon tubes connected each solution with a vessel filled with the corresponding solution, whilst into the latter vessels dipped the syphon tubes of calomel electrodes Great care was taken to prevent any access of potassium chloride to the solutions in contact with the membrane The usual precautions were taken to prevent undue intermixture of the various connecting solutions. The membrane vessel, calomel electrodes, and interconnecting syphons were immersed as far as possible in the water of a thermostat, which was kept at 25°.

The determination of the membrane potential difference was carried out as follows :—The E.M.F. of the cell

$$\overset{e_1}{\overbrace{\quad}} \qquad \overset{E_m}{\overbrace{\quad}} \qquad \overset{e_2}{\overbrace{\quad}}$$
$$\text{Cal.} \mid \text{K}_4\text{Fe(CN)}_6 \parallel \text{K}_4\text{Fe(CN)}_6 \mid \text{Cal} \qquad\qquad \text{(A)}$$
$$\text{(1)} \qquad\qquad \text{(2)}$$
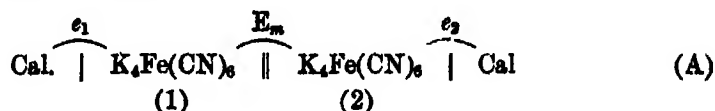
(in which the calomel electrodes are indicated by the abbreviation Cal , and the membrane by the symbol ‖), is constituted by the three potential differences e_1, e_2, and E_m, the latter being the sought-for " membrane-potential "

Suppose, now, the membrane removed and the following cell measured—

$$\overset{e_1}{\overbrace{\quad}} \qquad \overset{E_d}{\overbrace{\quad}} \qquad \overset{e_2}{\overbrace{\quad}}$$
$$\text{Cal.} \mid \text{K}_4\text{Fe(CN)}_6 \mid \text{K}_4\text{Fe(CN)}_6 \mid \text{Cal.} \qquad\qquad \text{(B)}$$
$$\text{(1)} \qquad\qquad \text{(2)}$$

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* *Cf* Walden, 'Zeitschrift für Physikal. Chemie,' vol. 10, p. 699 (1892)

† In one case this impermeability was tested over a period of four months.

E_d denoting the ordinary "diffusion-potential" between the solutions (1) and (2)   Then, if Δe denote the difference between the E.M.F.'s of cells A and B,

$$\Delta e = E_m - E_d,$$

and therefore

$$E_m = \Delta e + E_d.$$

In order to determine E_m, it is therefore necessary to calculate E_d This can be done by means of the equation

$$E_d = \frac{RT}{F}\left(u - \frac{v}{4}\right)\log\frac{a_1 c_1}{a_2 c_2},$$

where c_1, c_2, are the equivalent concentrations of the two solutions of potassium ferrocyanide, a_1, a_2, their corresponding degrees of ionisation, and u, v, the (mean) transport numbers of K and $\frac{1}{4}Fe(CN)_6$.   In this equation E_d denotes the excess of the positive potential of solution (2) over that of solution (1).

The values of a_1 and a_2 were taken from the conductivity data of Noyes and Johnston.[*]

An uncertainty, however, arises here, as this calculation assumes that the salt ionises only according to the equation

$$K_4Fe(CN)_6 \rightleftharpoons 4K + Fe(CN)_6''''.$$
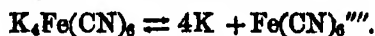
Such an assumption will be the more justified the diluter the solutions are

A further uncertainty relates to the evaluation of u and v, since the transport numbers of potassium ferrocyanide have not been sufficiently investigated.   We have therefore been obliged to calculate u and v by means of the equation $u = U/(U+V)$ and $v = V/(U+V)$, where U and V are the equivalent ionic conductivities of the potassium and ferrocyanogen ions in dilute aqueous solution at 25°   For this purpose we have taken

$$U_K = 74.5, \qquad V_{\frac{1}{4}Fe(CN)_6} = 111.0,$$

from the data of Noyes and Johnston for extreme dilution, whence follow the values

$$u = 0.404, \qquad v = 0.596.$$

The values of a as determined by the work of Noyes and Johnston for the concentrations employed by us are given in the following Table, the concentrations being expressed in gramme-equivalents per litre

<div align="center">Table I.—Ionisation of $K_4Fe(CN)_6$ at 25°.</div>

Concentration ...	1·0	0 1	0·05	0·04	0·02	0·0125	0·01	0·005
$100 a$..	40	53	58 6	60·4	67 0	70·7	73·5	79·5

* Noyes, 'Amer. Chem. Soc. Journ.,' vol. 30, p 351 (1908); Johnston, *ibid.*, vol. 31, p. 1010 (1909).

The membranes were tested to see if any potential difference existed across them when separating two solutions of potassium ferrocyanide of the same concentration It was found that within the error of measurement no such potential difference existed

The electromotive force was measured by means of a simple metre slide bridge and sensitive galvanometer, the precision of reading being at most 0 2 millivolt

Contrary to expectation, constancy of electromotive force was rapidly attained and preserved over an extended period of time. This is illustrated by the following Table (time indicates duration in hours from the setting up of the cell)

Table II.—Solutions N/1 and N/10 $K_4Fe(CN)_6$.

Time	$E_M + \Sigma e$.	$E_d + \Sigma e$	Δe	E_d (calc)	$E_M = \Delta e + E_d$
$\frac{1}{2}$	1 1198	1 0970	0 0228		0 0359
$1\frac{1}{4}$	1 1200	1 0970	0 0230		0 0361
$2\frac{1}{4}$	1 1204	1 0970	0 0234		0 0365
$4\frac{1}{4}$	1 1207	1 0970	0 0237		0 0368
$5\frac{1}{4}$	1 1207	1 0970	0 0237	0 0131	0 0368
25	1 1205	1 0970	0 0235		0 0366
27	1 1201	1 0970	0 0231		0 0362
28	1 1203	1 0970	0 0233		0 0364
29	1 1203	1 0970	0 0233		0 0364
32	1 1205	1 0970	0 0235		0 0366

It will be seen that the variation of E M F observed is well within the error of measurement.

The following Table contains the experimental results, concentrations being given as before in gramme-equivalents per litre.

Table III.—Experimental Data, 25°

Concentrations in apposition	$E_M + \Sigma e$	$E_d + \Sigma e$	Δe	E_d (calc)	$E_M (= \Delta e + E_d)$.
	volts	volts.	volt	volt	volt.
N ‖ 0 1 N	1 1207	1 0970	0 0237	0 0132	0 0369
N ‖ 0 05 N	1 1323	1 1012	0 0311	0 0171	0 0482
N ‖ 0 02 N	1 1508	1 1064	0 0444	0 0222	0 0666
N ‖ 0 01 N	1 1636	1 1111	0 0525	0 0262	0 0787
0 1 N ‖ 0 05 N	1 0886	1 0776	0 0110	0 0039	0 0149
0 1 N ‖ 0 04 N	1 0917	1 0773	0 0144	0 0051	0 0195
0 1 N ‖ 0 02 N	1 1053	1 0808	0 0245	0 0090	0 0335
0 1 N ‖ 0 0125 N	1 1144	1 0838	0 0306	0 0117	0 0423
0 1 N ‖ 0 01 N	1 1176	1 0839	0 0337	0 0129	0 0466
0 1 N ‖ 0 005 N	1 1294	1 0894	0 0400	0 0170	0 0570

The next Table shows the comparison between the values of E_M as determined in the manner explained and as calculated from equation (1)

Table IV —Comparison of Results, 25°

Concentrations in apposition	E_d	E_M from Table III	E_M from Equation (1)	Difference
				per cent
N ‖ N/10	0 0132	0 0369	0 0519	28 9
N ‖ N/20	0 0171	0 0482	0 0671	28 2
N ‖ N/50	0 0222	0 0666	0 0872	23 6
N ‖ N/100	0 262	0 0787	0 1026	23 3
N/10 ‖ N/20	0 0039	0 0149	0 0152	2 0
N/10 ‖ N/25	0 0051	0 0195	0 0201	3 0
N/10 ‖ N/50	0 0090	0 0335	0 0353	5 1
N/10 ‖ N/80	0 0117	0 0423	0 0459	7 8
N/10 ‖ N/100	0 0129	0 0466	0 0507	8 1
N/10 ‖ N/200	0 0170	0 0570	0 0665	14 3

The fifth column in Table IV gives the differences between values of E_M contained in columns 3 and 4 expressed as percentages of the values given in column 4

There is a large and fairly constant percentage deviation in all the measurements involving the equivalent normal solution of potassium ferrocyanide. Undoubtedly a large part of this must be ascribed to great uncertainty as to the correct values of the transport numbers and the degree of ionisation of this relatively strong solution   In the measurements involving no solution stronger than N/10 (lower portion of Table IV), there is a better agreement, though there is undoubtedly a tendency for the percentage deviation to increase as the ratio of dilution increases   In the case of the pairs N/10 ‖ N/20, N/10 ‖ N/25, and N/10 ‖ N/50, the percentage deviation is not more than would be expected from the errors of measurement   On referring to Table III it will be seen that the percentage deviation increases as the proportion that E_d plays in the determination of E_M ($E_M = \Delta e + E_d$) increases   It seems probable, therefore, that a large part of the deviation is to be ascribed to uncertainty in the calculation of E_d

It must also be remembered that even if the values of E_d were accurately known there might still occur deviation due to uncertainty as to the degree and nature of the ionisation of the potassium ferrocyanide and to deviation from the laws of ideal solution   Taking these various points into consideration, it seems very probable that the potential difference between two

aqueous solutions of potassium ferrocyanide separated by a membrane of colloidal copper ferrocyanide is given by the equation—

$$\pi_2 - \pi_1 = \frac{RT}{F} \log \frac{a_1}{a_2}, \tag{11}$$

where a_1 and a_2 are the "activities" of the potassium ion in the two solutions It will be observed that equation (11) reduces to equation (1) when the concentrations of the potassium ions are proportional to their activities

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Morphological Studies of Benzene Derivatives. VI—Para-sulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyanobenzene.

By C. S Mummery, B Sc

The compounds described in this communication were examined in order to contrast the para-mono-derivatives of benzenesulphonic acid with the di-derivatives studied by Colgate and Rodd * It is unnecessary to describe the methods used in preparing them, as these are well known.

The melting points of the various compounds are given in the following Table :—
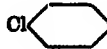
1	4				
	SO_2Cl	SO_2Br	SO_2NH_2	$SO_2NH\,Ph$	$SO_2NH\,C_6H_4\,CH_3$
Cl ..	53·5°	56°	143 5°	104°	87°
Br	74·5	77	165	118	94
I	84	97	190	143	129
CN	109	—	167	—	—

It is noticeable that the substitution of one halogen for another in the sulphonic radicle makes but a small difference in the melting point (about 3°) in comparison with that produced (about 20°) by a similar substitution in the nucleus.

In the case of the sulphochlorides and of the sulphonamides, the

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crystallographic constants of similar compounds containing different halogens are practically identical :—

Compound	Axial ratios			β
	a	b	c	
Cl⟨⟩SO$_2$Cl	0·840	1	2·079	83° 31′
Br⟨⟩SO$_2$Cl	0·820	1	2 074	83 13
I⟨⟩SO$_2$Cl	0·839	1	2·074	84 38
Cl⟨⟩SO$_2$NH$_2$	0·629	1	0·603	82 12
Br⟨⟩SO$_2$NH$_2$	0·628	1	0 601	81 4

Parachlorobenzenesulphochloride, $C_6H_4Cl\,SO_2Cl$ —This compound was obtained in measurable crystals from a mixture of benzene and light petroleum. Some difficulty was experienced in producing crystals which had sufficient forms for calculation

System . Monosymmetric.

Axial ratios $a:b$ $c = 0\cdot840 : 1$ $2\,079$ $\beta = 83°\,31′$

Forms observed {001}, {101}, {10$\bar{1}$}, {011}.

Angle	No of observations	Limits	Mean	Calculated
001 ː 10$\bar{1}$	27	116° 52′—117° 51′	117° 29′	—
101 10$\bar{1}$	22	43 31 — 44 8	43 49	—
001 011	41	63 42 — 64 39	64 11	—
001 $\bar{1}$01	29	62 6 — 63 0	62 26	62° 30′
011 01$\bar{1}$	31	51 6 — 51 49	51 32	51 37
011 $\bar{1}$01	33	77 51 — 78 53	78 19	78 24
011 10$\bar{1}$	32	101 20 —101 58	101 40	101 36

Several crystals of a labile modification were also deposited, but sufficient measurements for the calculation of their constants were not obtained.

Parachlorobenzenesulphobromide, $C_6H_4Cl.SO_2Br$.—Considerable difficulty was experienced in crystallising this substance in measurable form : it was eventually obtained from a mixture of benzene and light petroleum

System Monosymmetric.

Axial ratios a b $c = 1·901 : 1 : 1 527$ $\beta = 88° 26'$.

Forms observed· {100}, {101}, {$\bar{1}$01}, {110}.

Angle	No of observations	Limits	Mean	Calculated
100 $\bar{1}$01	15	129° 21'—130° 11'	129° 43'	—
100 110	36	61 47 — 62 35	62 14	—
100 101	9	51 57 — 52 31	52 11	—
101 110	13	72 21 — 72 56	72 37	72° 41'
110 $\bar{1}$10	21	55 13 — 55 59	55 34	55 32
101 $\bar{1}$01	6	77 14 — 77 57	77 30	77 32
$\bar{1}$01 : $\bar{1}$00	23	49 59 — 50 41	50 20	50 17
110 $\bar{1}$01	13	107 1 —107 41	107 21	107 19

Several crystals of a labile modification were also deposited but sufficient measurements for the calculation of their constants were not obtained

Parachlorobenzinesulphonamide, $C_6H_4Cl\ SO_2\ NH_2$ — Measurable crystals were deposited from a solution in acetone, crystals of one crop gave an electric discharge from opposite ends of an axis

System· Monosymmetric

Axial ratios a b $c = 0 629 : 1 : 0 603$ $\beta = 82° 12'$

Forms observed   {100}, {010}, {121}, {012}, {210}, {$\bar{1}$11}

Angle	No of observations	Limits	Mean	Calculated
010 : 210	22	72° 14'—73° 10'	72° 36'	—
010 012	19	73 1 —73 49	73 23	—
012 : $\bar{1}$00	11	82 15 —82 57	82 32	—
010 : $\bar{1}$11	23	67 5 —67 59	67 39	67° 35'
$\bar{1}$11 $\bar{1}$$\bar{1}$1	9	44 27 —45 19	44 48	44 50
210 2$\bar{1}$0	11	34 16 —35 4	34 48	34 44
012 · 0$\bar{1}$2	9	32 57 —38 59	33 27	33 14
100 : 012	11	97 4 —97 57	97 26	97 28
210 : 100	11	16 40 —17 45	17 19	17 22
010 : 121	21	46 30 —47 36	47 4	47 9
121 : 1$\bar{2}$1	12	85 55 —86 29	86 3	85 43

The corresponding anilide was obtained but not in measurable crystals , it closely resembles the corresponding bromanilide.

Parachlorobenzenesulphoparatoluidide, $C_6H_4Cl\ SO_2.NH\ C_6H_4.CH_3.$—Measureable crystals were obtained from a solution in ethylic acetate.

System Anorthic

Axial ratios $a · b : c = 1 020 . 1 · 1·096$

$\alpha = 106° 6'.$ $\beta = 93° 50'$ $\gamma = 77° 29'$

Forms observed   {100}, {001}, {010}, {101}, {10$\bar{1}$}, {11$\bar{1}$}, {01$\bar{1}$}

Angle	No of observations	Limits	Mean	Calculated
100　010	26	74° 0'— 74° 46'	74° 21'	—
010　00Ī	21	101 36 —102 19	101 56	—
001　01Ī	18	55 7 — 55 47	55 31	—
100　00Ī	17	89 20 — 89 49	89 36	—
100　10Ī	17	42 0 — 42 43	42 19	—
100　01Ī	9	76 16 — 76 48	76 30	76° 33'
010 : 10Ī	9	86 17 — 86 48	86 27	86 31
011　010	16	46 2 — 46 43	46 25	46 25
010　001	17	77 47 — 78 24	77 58	78 4
010　Ī00	25	105 13 —105 59	105 39	105 39
100 : 11Ī	12	43 4 — 43 36	43 18	43 4
01Ī　Ī00	8	103 12 —103 27	103 20	103 27
11Ī　01Ī	8	33 16 — 33 35	33 23	33 29
010　11Ī	6	49 53 — 50 21	50 5	50 24
11Ī : 10Ī	5	35 41 — 36 36	36 7	36 7
10Ī　0Ī0	5	93 1 — 94 6	93 34	93 29
100　001	17	90 9 — 90 57	90 21	90 24
10Ī : 00Ī	16	46 59 — 47 41	47 17	47 17
100　101	9	42 25 — 43 17	42 51	—
101 : 001	6	47 16 — 47 50	47 34	—

Parabromobenzenesulphochloride, $C_6H_4Br.SO_2Cl$.—Measurable crystals were obtained from a mixture of benzene and light petroleum

System · Monosymmetric.

Axial ratios　$a\ b : c = 0\ 820 : 1\ 2074\quad \beta = 83'\ 13'.$

Forms observed　{001}, {10Ī}, {011}, {012}

Angle	No of observations	Limits	Mean	Calculated
101　10Ī	12	42° 27'— 43° 12'	42° 57'	—
10Ī : 001	24	116 44 —117 36	117 21	—
001　011	41	63 40 — 64 28	64 6	—
001　Ī01	21	62 32 — 63 15	62 47	62° 39'
011　Ī01	33	77 52 — 78 54	78 34	78 27
011　10Ī	36	101 1 —101 56	101 28	101 33
011 : 01Ī	19	51 24 — 52 11	51 42	51 43
011 : 012	5	17 53 — 18 5	18 0	18 17
012 : 001	7	45 23 — 46 14	45 58	45 49

The corresponding bromide was not obtained in measurable form

Parabromobenzenesulphonamide, $C_6H_4Br\ SO_2.NH_2$.—This amide was obtained in measurable form from a solution in acetone.

System . Monosymmetric

Axial ratios : $a : b\ c = 0\cdot 628\cdot 1\ 0\cdot 601\quad \beta = 81°\ 4'.$

Forms observed · {100}, {101}, {210}, {111}, {121}, {012}, {Ī11}.

Angle		No of observations	Limits		Mean		Calculated	
010	2I0	46	72° 12'—78° 16'		72	46	—	
010	012	36	73 4 —73 58		73	27	—	
012	I00	12	81 6 —81 48		81	26	—	
012	0I2	20	32 44 —33 31		33	6	33°	6'
2I0	100	26	16 43 —17 46		17	13	17	14
100	012	11	98 12 —98 59		98	34	98	34
210 : 2I0		13	34 5 —34 51		34	30	34	26
010	121	65	46 3 —47 25		46	50	46	57
121	1$\bar{2}$1	32	85 52 —86 54		86	14	86	6
010	I11	45	67 49 —68 49		68	11	69	13
I11	I$\bar{1}$1	21	43 1 —43 54		43	33	43	34
111	121	2	17 56 —18 1		17	58	18	1
111	101	2	24 32 —25 2		24	47	25	2
12I	101	2	42 59 —43 30		43	14	43	3

An electric discharge from opposite ends of an axis was obtained from crystals of several crops of this substance

Parabromobenzenesulphanilide, $C_6H_4Br\ SO_2\ NH\ C_6H_5$.—This substance forms hemimorphic, orthorhombic crystals of very peculiar habit the measurements are therefore withheld until it has been submitted to further study.

The corresponding paratoluidide appears to resemble the corresponding chloro-derivative very closely

Pariodobenzenesulphonic chloride, $C_6H_4I\ SO_2Cl$ —This chloride was deposited in measurable crystals from a mixture of benzene and light petroleum.

System Monosymmetric

Axial ratios $a\quad b\quad c = 0\,839\quad 1\quad 2\,074\quad \beta = 84°\ 38'$

Forms observed. {001}, {10$\bar{1}$}, {111}, {011}, {012}

Angle		No of observations	Limits		Mean		Calculated	
001 · 011		28	63° 43'— 64° 37'		64°	8'	—	
011 · 10$\bar{1}$		21	101 5 —101 55		101	16	—	
10$\bar{1}$	111	14	55 29 — 56 18		55	49	—	
011 : I01		22	78 35 — 78 57		78	44	78°	44'
011	012	7	18 2 — 18 21		18	9	18	4
012 : 001		7	45 39 — 46 4		45	53	45	54
001	10$\bar{1}$	18	116 22 —116 46		116	28	116	36

The bromide, amide, anilide, and paratoluidide of the iodo-acid were also prepared, but not obtained in measurable form.

Cyanobenzeneparasulphonic acid.—This acid was prepared by Remsen, Hartmann and Muckenfuss[*] from the parasulphonamide of benzoic acid. It is more easily prepared from diazobenzenesulphonic anhydride by

[*] 'Amer. Chem Journ,' 1896, p 150.

treatment with cuprous potassium cyanide The method adopted was as follows · 17 grm of sulphanilic acid were diazotised by sodium nitrite in the usual way, the diazo-compound was then made into a sludge with water and added slowly to a previously prepared *cold* solution of cuprous cyanide (made by adding gradually a hot solution of 56 grm of potassium cyanide in 200 c c water to a boiling solution of 32 grm of crystallised copper sulphate in 200 c.c water) It was found to be important to keep the temperature below 20° while adding the diazo-compound Finally, the cold mixture was acidified with hydrogen chloride (to decompose the cyanides) until no further precipitate of cuprous cyanide was produced The solution was boiled to remove hydrogen cyanide and the liquid concentrated after the cuprous cyanide had been filtered off The solid product was extracted with hot methylated spirit, in which the potassium cyano-sulphonate is soluble. The amount of sulphonate finally obtained as a crystalline, almost colourless salt was about 70 per cent of the theoretical amount calculated from the diazo-compound

Paracyanobenzenesulphochloride, $C_6H_4(CN)SO_2Cl$ —This chloride crystallises readily in measurable form from benzene

(Found Cl (sulphonic) 17 6 per cent , N 7 per cent , $C_6H_4CN SO_2Cl$ requires Cl (sulphonic) 17 59 per cent., N 6 93 per cent)

System Orthorhombic.

Axial ratios $a : b \quad c = 1 139 · 1 \quad 1 709$

Forms observed . {001}, {111}, {110}

Angle	No of observations	Limits		Mean	Calculated
001 : 111	35	42° 43'—	43° 29'	43° 5	43° 4'
111 110	47	46 36 —	47 20	46 56	—
110 : I11	23	105 4 —	105 35	105 14	—
110 : 1I1	22	74 36 —	74 59	74 46	74 46
110 1I0	12	67 4 —	67 43	67 22	67 22
110 I10	12	112 18 —	112 50	112 33	112 33

Paracyanobenzenesulphonamide, $C_6H_4(CN).SO_2.NH_2$ —This amide crystallises readily in measurable form from acetone, it is easily soluble in hot water

System · Orthorhombic

Axial ratios $a \quad b . c = 0 793 : 1 : 0·537$

Forms observed   {010}, {110}, {011}, {101}.

Angle	No of observations	Limits		Mean		Calculated	
010 : 011	82	51° 18'— 52° 14'		51° 35'		—	
011 101	16	63 40 — 64 10		63 55		—	
011 0Ī1	20	76 26 — 77 2		76 48		76° 50'	
011 Ī0Ī	15	115 45 —116 27		116 9		116 5	
101 Ī01	7	67 40 — 68 28		68 8		68 16	
101 10Ī	8	111 30 —112 16		111 53		111 44	

Crystals of this substance, like those of the other amides measured, gave an electric discharge from opposite ends of an axis

The magnesium salts of the three acids containing halogen were also prepared in order to compare them with the benzene- and dichlorobenzene-sulphonates considered in Part IV. The structure of these and the corresponding ferrous and cobalt salts is discussed in Part VII

Well developed crystals of the three salts were obtained in the form of thick prisms by the slow evaporation of aqueous solutions at 25° C. All three salts are closely isomorphous and contain six molecular proportions of water of crystallisation

$(C_6H_4BrSO_3)_2Mg\ 6H_2O$ —Water found 18 55 per cent , calc 17·88 per cent
$(C_6H_4ISO_3)_2Mg\ 6H_2O$ —   „   14 89   „   „   15 47   „

A determination of Mg in the dehydrated Br-salt gave 4 95 per cent. Mg
The formula $(C_6H_4Br\ SO_3)_2\ Mg$ requires 4 90 per cent Mg

Magnesium parachlorobenzenesulphonate, $(C_6H_4Cl\ SO_3)_2Mg\ 6H_2O$.—
System : Monosymmetric
Axial ratios · a b · $c = 3\ 6870\ .\ 1\ \ 0\ 9223.$ $\beta = 93°\ 12'$.
Forms observed $a\{100\}, r\{101\}, s\{\bar{1}01\}, d\{301\}, m\{110\}, n\{310\}, q\{011\}$

Angle	No of observations	Limits		Mean		Calculated	
100 : 310	16	50° 40'— 51° 4'		50° 52'		—	
310 : 110	2	23 54 — 23 59		23 56		23° 54'	
310 : 310	9	77 56 — 78 24		78 13		78 16	
101 : 310	11	79 12 — 79 33		79 19		—	
310 : Ī0Ī	11	100 29 —100 46		100 40		100 39	
100 : 301	8	51 6 — 51 58		51 10		51 21	
301 : 101	8	21 12 — 21 41		21 34		—	
100 . 101	9	72 32 — 53 10		72 44		72 55	
101 : Ī01	6	27 28 — 28 0		27 41		27 34	
101 : Ī00	6	106 56 —107 24		107 6		107 5	
Ī01 : Ī00	5	79 11 — 79 33		79 25		79 31	
101 : 011	1	——		44 0		44 20	
011 : Ī10	1	——		50 30		50 6	
Ī10 : Ī0Ī	1	——		85 26		85 34	
310 : Ī10	1	——		54 35		54 32	

Magnesium parabromobenzenesulphonate (C₆H₄Br.SO₃)₂Mg.6H₂O —
System Monosymmetric

Axial ratios a $b \cdot c = 3\,7380$ 1 0·9094 $\beta = 93°\ 51'$.

Forms observed $a\{100\}$, $r\{101\}$, $s\{\bar{1}01\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$.

Angle		No. of observations	Limits				Mean		Calculated	
100	310	31	51°	1′—	51°	50′	51°	15′	—	
310	110	16	28	27 —	28	51	28	41	28°	46′
310 ; 310		9	77	28 —	77	45	77	37	77	30
310	Ī10	11	53	43 —	54	4	53	52	53	44
110	Ī10	3	30	12 —	30	18	30	14	29	58
101	310	17	79	7 —	79	30	79	17	—	
310 ; 10Ī	16		100	30 —	100	49	100	40	100	43
100	101	8	72	28 —	73	10	72	46	72	43
101	Ī01	8	107	24 —	107	35	107	14	107	17
101	011	11	43	49 —	44	10	43	58	—	
011	Ī10	9	50	17 —	50	32	50	25	50	24
Ī10	10Ī	8	85	36 —	85	55	85	45	85	36
Ī10	101	7	94	8 —	94	26	94	19	94	22

Magnesium pariodobenzenesulphonate, (C₆H₄I SO₃)₂Mg 6H₂O —
System Monosymmetric

Axial ratios a b $c = 3\,7965$ 1 0 9148 $\beta = 93°\ 1'$

Forms observed $a\{100\}$, $r\{101\}$, $d\{301\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$.

Angle		No. of observations	Limits				Mean		Calculated	
100	310	17	51°	26′—	51°	50′	51°	41′	—	
310	110	11	28	26 —	28	36	28	31	28°	34′
310	310	5	76	32 —	76	38	76	36	76	38
310	Ī10	11	52	58 —	53	10	53	2	53	4
110	Ī10	4	29	27 —	29	36	29	30	29	30
100	101	5	73	34 —	73	40	73	37	—	
100	301	8	52	10 —	52	45	52	25	52	10
301	101	8	21	15 —	21	28	21	20	21	27
101	Ī00	8	106	16 —	106	23	106	20	106	23
301	310	10	67	27 —	67	46	67	39	—	
310	01Ī	10	52	18 —	52	45	52	29	52	42
01Ī	30Ī	10	59	43 —	59	56	59	50	59	39

Morphological Studies of Benzene Derivatives —VII. The Correlation of the Forms of Crystals with their Molecular Structure and Orientation in a Magnetic Field in the Case of Hydrated Sulphonates of Dyad Metals.

By HENRY E ARMSTRONG, F.R S , and E H RODD, D Sc

In Part V of these Studies[*] much evidence was adduced showing that a close relationship is traceable between the substituted sulphonic chlorides and bromides generally of the form $C_6H_3R_1R_2 SO_2X$, as these may all be referred to equivalence parameters, varying between narrow limits, similar in two directions to those deduced for benzene itself, the change in the third being such as may be expected to follow from the introduction of the group SO_2X

It is obviously desirable to consider also cases in which X is a more complex radicle than either Cl or Br A few of these have been discussed in Part V Certain benzenesulphonates were considered in two previous communications of the series [†] apparently the results justify conclusions in harmony with those arrived at in the case of the simple sulphochlorides and bromides But in view of the marked influence which halogens exert on the properties of the benzenesulphonic acids and of the manner in which the amount of " water of crystallisation " often varies as the metal is varied, it appeared to be desirable to study sulphonates generally as systematically as sulphonic chlorides and bromides have been studied

We have directed our attention specially, in the first instance, to salts of dyad metals, on account of the observations made with reference to these salts in Part IV—for the following reasons Of late years much attention has been paid to the so-called complex salts, particularly by Werner, who has obtained results of very special interest. Such salts are formed with peculiar readiness by metals of the iron group The formulæ which Werner has introduced, though satisfactory up to a certain point as symbolic

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[*] " Morphological Studies of Benzene Derivatives V —The Correlation of Crystalline Form with Molecular Structure : a Verification of the Barlow Pope Conception of 'Valency-Volume,'" by Henry E Armstrong, R. T Colgate and E H Rodd, 'Roy. Soc Proc ,' A, vol. 90, pp. 111–173

[†] " III —Paradibromobenzenesulphonates (Isomorphous) of the 'Rare Earth' Elements— a Means of determining the Directions of Valency in Tervalent Elements," by Henry E. Armstrong and E. H. Rodd, ibid., vol. 87, pp. 204–217 ; " IV —The Crystalline Form of Sulphonates in Relation to their Molecular Structure," by E H Rodd, ibid., vol. 89, pp. 292–313.

expressions of the chemical behaviour of the salts, cannot be regarded as satisfactory or perhaps even as possible representations of their molecular structure We stand urgently in need of special methods of determining structure in such cases, the study of salts formed by the metals referred to in various ways is therefore of particular interest

We have represented (No. IV, p 310) the structure of sulphonates of the dyad metals provisionally in the manner shown in fig 1, in which the shaded portion represents the region occupied by the sulphonic radicles and the water of crystallisation, the metal being at the "centre" of the system *
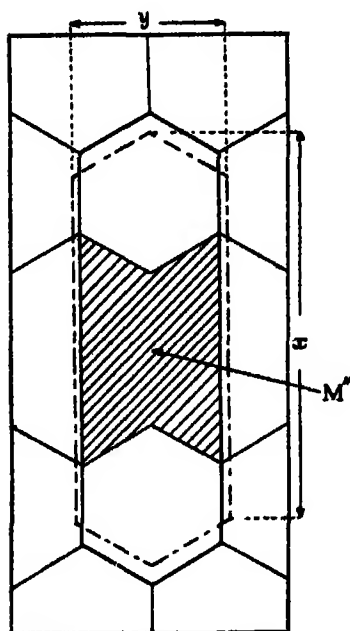
Fig 1.

Assuming the metallic atom to be placed at the "centre" of the system in the manner shown, it appeared probable that the direction in which the metallic atoms were stacked in the crystal might prove to be one having special properties, in the case of a magnetic metal such as iron, for example We had in mind Faraday's demonstration of "magnecrystallic polarity" in various substances, notably in ferrous sulphate

In the expectation that the z parameter would prove to be such an axis, we determined the effect of a magnetic field on several ferrous sulphonates. On suspending the crystals between the poles of a magnet of moderate strength, so that one or other of the three axial directions was in a vertical position, the direction of maximum magnetic permeability was found to be along x when the crystal was suspended with either y or z vertical, and along y when x was vertical, therefore at right angles to the z parameter In the case of ferrous sulphate, as stated by Faraday, we found that the crystal was affected specially in only one direction. On examining salts of the other magnetic metals, however, we found their magnetic behaviour to be so different from that of the iron salts that we have been led to devote our attention more particularly to the problem thus disclosed, especially as the property referred to has proved to be of unexpected significance as an aid to the interpretation of crystalline form.

* It is necessary to make slight changes in the figure if it is to correspond to the values given later on (p. 489).

In our experiments the comparison has always been made between strictly isomorphous salts The salts compared have been sulphates, double sulphates of ammonium and the dyad metals, benzene- and toluene-sulphonates, parachloro-, parabromo- and pariodobenzenesulphonates. Certain other salts of different type have also been examined tentatively.

Hitherto we have made only qualitative observations It so happened that the magnet with which we made our first experiments affected iron and cobalt salts readily but was without perceptible action on the corresponding salts of zinc and magnesium and even on those of manganese , salts of nickel were but slightly affected, as were those of copper and to about an equal extent The salts that were unaffected by this magnet could be directed by a stronger field

The electromagnet used has flat poles facing one another, 6 4 cm. apart , it was found necessary, however, to concentrate the field by facing each pole with a rectangular block of soft iron, thus reducing the distance between the poles to 1 9 cm The flux density of the field used was 2400 lines per square centimetre The area of the face of each pole (7·7 × 4 75 cm) was such that the field between them must have been sensibly uniform The crystal to be examined was suspended, so that free rotation was possible, from a suitable support, by a single strand of artificial silk fastened by means of a hook of copper wire to a paper stirrup The crystal could be fixed in any desired position upon the stirrup by means of a tiny pellet of plasticine or vaseline

Faraday's original observations were made with bismuth and were subsequently extended to ferrous sulphate and a few other substances. At about the same time, Plücker carried out similar experiments principally with minerals.

Faraday formed the opinion that crystals possess what he termed a magnecrystallic axis In some cases, this axis set along the lines of force— *axially*, in others at right angles to the lines of force—*equatorially*, ferrous sulphate, a magnetic salt, behaved in the former manner , bismuth, a strongly diamagnetic substance, in the latter [*]

Plücker was of opinion that a definite relationship was traceable between the magnetic and the optical properties of crystals. His views were adversely criticised by Knoblauch and Tyndall[†] and at a later date, Grailich

[*] 'Electrical Researches,' 1848–1850, xxii, xxiii, xxvi.

[†] 'Phil. Mag.,' 1850, p. 1 The whole of Tyndall's work (1850–1856) on the subject is published in a special volume, 'Diamagnetism and Magnecrystallic Action' (Longmans, Green and Co., London)

and von Lang* also came to the conclusion that there is no obvious relation-
ship between the optical and magnetic properties of crystals.

According to Knoblauch and Tyndall, a relationship exists between the
direction of the cleavage plane of a crystal and the manner in which it sets
in the magnetic field , all the crystals they examined, whether paramagnetic
or diamagnetic, set in a definite manner when the field was sufficiently
powerful   In the case of paramagnetic substances, the cleavage plane set in
the axial plane, *i e* with the perpendicular thereto across the lines of force ,
whilst in that of diamagnetic substances this plane was found to set in the
equatorial plane, with its perpendicular along the lines of force from pole to
pole   Of the few examples adduced in support of this view, the most
striking are those afforded by the isomorphous sulphates of magnesium, zinc
and nickel , the first two are diamagnetic and set with the cleavage plane
equatorially   the last is paramagnetic and sets with its cleavage plane
axially

The first crystal which we examined, one of ferrous toluenepaiasulphonate,
proved to be an exception to the principle enunciated by Knoblauch and
Tyndall, as it set with its cleavage plane in the equatorial plane, a behaviour
characteristic, according to them, of diamagnetic substances   Many similar
exceptions were subsequently discovered   Even ferrous sulphate sets with
its cleavage plane in the equatorial plane, a fact unaccountably overlooked
by Tyndall, Faraday having described its behaviour in the magnetic field as
accurately as was possible without mentioning crystallographic details   To
judge from our observations, the direction of maximum permeability in para-
magnetic substances may lie either in the cleavage plane or perpendicular
thereto and in some cases, the cleavage plane sets either axially or equa-
torially according to the direction in which the crystal is suspended.
Apparently no simple relationship obtains between the cleavage plane and
the magnetic properties of crystals   The apparent connexion no doubt arises
from the fact that both the direction of maximum permeability and the
cleavage plane or its perpendicular are important directions in the crystal
structure.

The only systematic attempt that has been made to determine the
orientation of crystals in a magnetic field with respect to their crystallo-
graphic axes appears to be that of Grailich and von Lang † These authors
examined over 30 orthorhombic substances, by suspending them successively
with the axes *a, b,* and *c* in the vertical position, then observing in each case
which of the other two axes set axially and which equatorially. Apparently,

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* 'Sitzungsber. Akad Wiss Wien,' vol. 33, p. 439 (1858).
† *Loc cit*, vol 32, p 43.

however, they chose their material in a haphazard manner consequently no general conclusions can be drawn from the observations. They devised a system of symbols to indicate the magnetic properties of a crystal If, in the case of a paramagnetic substance, the strongest tendency were for the axis *b* to set axially and if, when *b* was vertical, *a* set axially, the symbol π (bac) was given to the substance, π denoting a paramagnetic substance and the order of the letters the order in which the axes stand with respect to their power of transmitting the magnetic force In the case of diamagnetic substances, the symbol δ is used instead of π, the order of the letters indicating the power of transmitting "diamagnetic force," the first letter indicating which axis sets equatorially with the greatest force Not only is the assumption of two kinds of magnetic force, diamagnetic and paramagnetic, unwarranted but the system of symbols does not apply, in many cases, to monosymmetric crystals, which sometimes set with a direction between the crystallographic axes along or at right angles to the lines of force

The Magnetic Properties of Salts of Dyad Metals

For the purposes of this inquiry, we have specially prepared and measured iron, cobalt and nickel salts ' of benzenesulphonic, tolueneparasulphonic, parachloro-, bromo- and iodobenzenesulphonic and paradichlorobenzenesulphonic acids The observations made with these and other similar salts are recorded in this section

Ferrous sulphate, $FeSO_4 7H_2O$ —This salt is monosymmetric, the axial ratios are —

$$a \quad b \quad c = 1\ 1828 \quad 1 \quad 1\ 5427 \quad \beta = 104° 15\tfrac{1}{2}'$$

There is a perfect plane of cleavage parallel to $c\{001\}$,

When the crystal is suspended from any point in the zone *ab*, so that $c\{001\}$ is in a vertical plane, it sets very strongly with the face $c\{001\}$ parallel to the pole of the magnet, i e, in the equatorial plane , when suspended so that $c\{001\}$ is horizontal, the axis *b* sets axially but is weakly directed

Cobalt sulphate, $CoSO_4 7H_2O$ —This salt is isomorphous with ferrous sulphate.

$$a \cdot b \quad c = 1\ 1815 \quad 1\ .\ 1\ 5325 \quad \beta = 104° 40' \text{ (Marignac)}$$

The plane of cleavage is $c\{001\}$

When the crystal is suspended in the magnetic field with its cleavage plane vertical, this plane sets axially. In the case of ferrous sulphate, the cleavage plane sets equatorially

When the cleavage plane is horizontal, the axis *b* sets equatorially, the axis *a* setting in the axial direction.

Ferrous ammonium sulphate, $FeSO_4 (NH_4)_2SO_4.6H_2O$ —This substance has

recently been subjected to an exhaustive crystallographic examination by Tutton*, our measurements of well developed crystals, made before we became acquainted with Tutton's work, agree precisely with his

The double salt is monosymmetric, the axial ratios being —

$$a \; b \cdot c = 0.7377 \; 1 \; 0.4960 \quad \beta = 106° 50'.$$

The crystals cleave fairly readily parallel to $\imath\{\bar{2}01\}$

The behaviour of the crystals in a magnetic field is highly interesting The most important plane in the crystal (magnetically) is $r\{\bar{2}01\}$ So long as the crystal is suspended with $r\{\bar{2}01\}$ in a vertical plane, the crystal sets strongly with this plane in the axial plane, the perpendicular thereto setting across the lines of force If, however, the plane $r\{\bar{2}01\}$ be horizontal, the crystal sets weakly with the axis of symmetry b across the lines of force. On contrasting these results with the observations of St Meyer, as interpreted by Tutton†, upon the crystallisation of this salt in a magnetic field, it appears that tabular crystals are formed, growing on $\imath\{\bar{2}01\}$, which are all so deposited that the shorter diagonal, which is parallel to the plane of symmetry, coincides with the direction of the lines of force The crystals are therefore orientated precisely as they set when suspended in a magnetic field so that $r\{\bar{2}01\}$ is horizontal It may well be that such crystals are first formed floating freely in the liquid and are orientated before they take up a stationary position upon the bottom of the vessel

Our observations also raise anew the question, which was discussed by Tutton, as to the correct setting of crystals of this salt and of other members of the series G Wulff,‡ on account of the remarkable predominance of the form $r\{\bar{2}01\}$ in ferrous ammonium sulphate, considers this to be a fundamental form and proposes to make it the basal plane $c\{001\}$ Tutton, however, taking into account the complete isomorphous series to which this salt belongs, prefers to adhere to the original setting proposed by Murmann and Rotter§ Our observations, however, emphasize the importance of the plane $r\{\bar{2}01\}$ particularly in the cases of ferrous and of cobalt ammonium sulphate This evidence, together with the fact that the plane is the principal cleavage plane throughout the series, inclines us to prefer Wulff's setting Further discussion of this point must, however, be reserved

Cobalt ammonium sulphate, $CoSO_4(NH_4)_2SO_4 6H_2O$ —The axial ratios of this salt, according to Marignac, are —

$$a \cdot b \cdot c = 0.7392 \; 1 \cdot 0.4985 \quad \beta = 106° 56'.$$

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* 'Roy Proc. Soc.,' A, vol. 88, p. 36 (1913).

† *Op cit*, p. 365

‡ 'Zeits. für Kryst,' vol 34, p. 466 (1901).

§ 'Sitzungsber d Akad. d. Wiss. Wien,' vol. 34, p. 153 (1889).

We find the magnetic behaviour to be directly opposed to that of the isomorphous ferrous salt   The cleavage plane $r\{\bar{2}01\}$, when in a vertical plane, always sets in the equatorial plane very strongly with its perpendicular along the lines of force, when $r\{\bar{2}01\}$ is horizontal, the axis of symmetry b sets axially, along the lines of force

Cobalt ammonium selenate, $CoSeO_4 \cdot (NH_4)_2SeO_4 \, 6H_2O$ —This salt corresponds in magnetic behaviour with cobalt ammonium sulphate   The tendency of the axis b to set axially when $r\{\bar{2}01\}$ is horizontal seems, however, to be weaker than in the case of the sulphate   Such observations are evidence of the need of quantitative experiments in connection with the work

Nickel ammonium sulphate and Copper ammonium sulphate—These two isomorphous salts behave similarly when suspended in the magnetic field.

(1) When $c\{001\}$ is horizontal, the axis b sets equatorially

(2) When the plane $a\{100\}$ is horizontal (this face not being developed), the axis b sets axially

(3) When the axis b is vertical, the plane $a\{100\}$ sets in the equatorial plane

The point of interest about these observations is that, whereas in the case of the isomorphous ferrous and cobalt salts the plane $r\{\bar{2}01\}$ sets in the one case axially and in the other equatorially, in the nickel and copper salts this plane seems to have lost its influence on the setting of the crystals, as when b is vertical the plane $a\{100\}$ sets equatorially

Ferrous benzenesulphonate, $(C_6H_5SO_3)_2Fe \, 6H_2O$ —This salt crystallises from water in well developed tablets, of a pale green colour, generally growing on $a\{100\}$, thin in the direction of the a axis   The crystals are similar in appearance to those of cobalt tolueneparasulphonate (fig 3)   Sometimes growth takes place on $q\{011\}$ or $m\{110\}$, so that the crystals have a prismatic habit

One of the faces $a\{100\}$ generally gives multiple reflections, owing to the presence of vicinal faces   The reflections from the other forms are usually good, particularly from $q\{011\}$.

The cleavage is perfect parallel to $a\{100\}$.   Twinning occurs on $a\{100\}$

The crystals are affected even by a weak magnetic field, their behaviour, deduced from that of many specimens of different shapes and sizes, was very uniformly as follows —

Vertical axis	Setting in magnetic field	
	Axial	Equatorial
a	b	c
b	a	c
c	a	b

The axis a tends strongly to set axially   This is well shown on suspending the crystal with b horizontal and a inclined at various angles to the vertical, the tendency of a or its horizontal component to set axially then opposes the tendency of b to set axially, but b is always forced into the equatorial position until a is but slightly inclined to the vertical   Then, as a approaches closely to the vertical, the crystal sets with b in the axial position

When the axis a sets axially, the face $a\{100\}$, which is the cleavage plane, is in the equatorial plane   According to Knoblauch and Tyndall's rule, as the salt is paramagnetic, the cleavage plane should set in the axial plane

System   Monosymmetric

$a \quad b \quad \iota = 3 5690 \quad 1 \quad 1 1058 \quad \beta = 86° 18'$

Forms observed $a\{100\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, $s\{301\}$, $\sigma\{\bar{3}01\}$, and, rarely, $\rho\{101\}$

Angle	No of observations	Limits	Mean observed	Calculated
100 110	29	74° 11'—74° 30'	74° 19'	—
110 $\bar{1}$10	13	31 14 —31 26	31 22	31° 22'
100 310	20	49 41 —49 58	49 50¼	49 58½
310 110	13	24 21 —24 32	24 26	24 25¼
011 01$\bar{1}$	20	84 19 —84 25	84 22	—
01$\bar{1}$ 0$\bar{1}$$\bar{1}$	22	95 31 —95 48	95 38	95 38
100 : 011	22	92 11 —92 40	92 29	92 29
011 $\bar{1}$00	22	87 23 —87 45	87 31	—
100 301	8	49 0 —49 12	49 4½	40 5
$\bar{1}$00 301	10	44 51 —45 15	45 2	45 7
301 $\bar{1}$01	2	24 14 —24 28	24 21	24 19
301 011	6	61 22 —61 33	61 29	61 27
011 310	4	53 29 —53 32	53 30¼	53 30
310 301	4	64 51 —65 5	65 59	65 3
301 011	6	59 31 —59 44	59 38	59 39
011 : 310	3	57 23 —57 25	57 24	57 23
310 : 30$\bar{1}$	3	62 46 —62 59	62 53	62 58
110 011	5	45 20 —45 28	45 26	45 26
$\bar{1}$10 011	7	43 26 —43 34	43 30	43 31

Cobalt benzenesulphonate, $(C_6H_5SO_3)_2Co\ 6H_2O$ —This salt has the same general habit as the corresponding ferrous salt. The cleavage is perfect parallel to $a\{100\}$. Twinning occurs on $a\{100\}$.

The direction of greatest magnetic permeability is that of the *c* axis, which in the ferrous salt is the direction of least permeability

Vertical axis	Setting	
	Axial	Equatorial
a	*c*	*b*
b	*c*	*a*
c	*b*	*a*

It is to be noted that the direction of greatest permeability in this salt lies in the cleavage plane, whilst in the ferrous salt it is perpendicular to this plane   The cleavage plane, when vertical, sets in the axial plane

System   Monosymmetric

$a\ b\ c = 1\,5560 : 1\ 1\,1086\quad \beta = 86°\ 7'$

Forms observed $a\{100\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, $s\{301\}$, $\sigma\{\bar{3}01\}$, and, rarely, $r\{101\}$ and $\rho\{101\}$

Angle	No of observations	Limits	Mean observed	Calculated
100 110	18	74° 11′—74° 21′	74° 15½′	- -
110 1̄10	4	31 22 —31 35	31 28½	31° 29′
100 310	12	49 40 —49 54	49 45	49 47
310 110	9	24 24 —24 35	24 30	24 28½
011 01̄1	16	84 9 —84 21	84 14	84 14
01̄1 01̄1	17	95 38 —95 51	95 46	—
100 011	15	92 24 —92 42	92 36	—
011 1̄00	13	87 18 —87 31	87 24	87 24
100 301	5	48 41 —49 5	48 56	49 0
1̄00 301	4	44 50 —44 51	44 50½	44 51
301 101	1	——	27 10	27 15
301 1̄01	2	24° 19′	24 19	24 19¼
301 011	3	61 36 —61 38	61 37	61 38
3̄01 011	2	59 43 —59 45	59 44	59 44
101̄ 110	1	——	84 28	84 28
110 011	1	——	45 26	45 26
011 1̄01	1	——	50 7	50 6
1̄10 011	1	——	43 23	43 25½

Nickel benzenesulphonate, $(C_6H_5SO_3)_2Ni\ 6H_2O$ —This salt forms beautiful dark green crystals very similar in habit to those of the corresponding ferrous and cobalt salts

Cleavage perfect parallel to $a\{100\}$.

The crystals are affected by a magnetic field but very feebly in comparison with those of the ferrous and cobalt salts   It differs in behaviour from both of these.   The axis *b* is the direction of greatest permeability : when

suspended with b vertical, the axis a appears to set axially but with very feeble force

Vertical axis	Setting	
	Axial	Equatorial
a	b	c
b	a	c
c	b	a

System Monosymmetric

a b $c = 3\,5476$ 1 1 1076 $\beta = 86° 9'$

Forms observed $a\{100\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, $s\{301\}$, $\sigma\{\bar{3}01\}$, $r\{101\}$, and $\rho\{\bar{1}01\}$

Angle	No of observations	Limits		Mean observed	Calculated
100 110	17	74° 9'—74' 17'		74° 13'	74° 13¼'
110 1̄10	5	31 28 —31 36		31 30	31 33
100 310	28	49 33 —49 50		49 43	—
310 110	12	24 22 —24 34		24 28	24 30¼
011 01̄1	18	84 18 —84 21		84 17	—
01̄1 0̄1̄1	18	95 40 —95 50		95 43	95 43
100 011	26	92 30 —92 39		92 35	92 35
011 1̄00	26	87 18 —87 31		87 25	—
100 301	12	48 55 —49 3		48 59	48 56
1̄00 3̄01	10	44 42 —44 52		44 47½	44 50
100 101	1	———		76 13	76 12
100 1̄01	1	———		68 58	69 11
301 101	1	———		27 18	27 16
301 1̄01	1	———		24 11	24 21

Ferrous tolueneparasulphonate, $(C_6H_4CH_3SO_3)_2Fe.6H_2O$.—This salt crystallises generally in small square plates of a pale green colour, growing on $a\{100\}$ and truncated at the corners by $q\{011\}$ (fig 2)   Large crystals were not very easily obtained.

The cleavage is perfect parallel to $a\{100\}$ Twinning occurs on $a\{100\}$

The magnetic behaviour corresponds exactly with that of ferrous benzene-sulphonate

System Monosymmetric

a $b \cdot c = 3\,9972 : 1 . 1\,1051.$ $\beta = 88° 37'.$

Forms observed : $a\{100\}$, $m\{110\}$, $q\{011\}$, $s\{301\}$, $\sigma\{\bar{3}01\}$, $r\{101\}$, $\rho\{101\}$, and, rarely, $n\{310\}$ and $p\{210\}$.

Angle	No of observations	Limits		Mean observed	Calculated
100 : 110	47	75° 47' —76° 10'		75° 57'	—
110 1̄10	22	27 53 —28 13		28 6	28° 0'
011 01̄1	21	84 13 —84 24		84 18	—
01̄1 01̄1̄	21	95 28 —95 50		95 42	95 42
100 011	23	90 49 —91 2		90 55	90 55½
011 1̄00	23	89 0 —89 12		89 4½	—
100 301	10	51 0 —51 20		51 8	51 9
1̄00 301	10	49 25 —49 39		49 33	49 30
301 101	1	—		24 56	24 41
301 1̄01	6	23 27 —23 54		23 42	23 46
110 301	4	98 43½ —99 23		98 54	99 4
301 1̄10	4	80 43 —81 17		81 5	80 56
110 011	5	44 14 —44 20		44 17	44 20½
011 1̄01	4	49 38 —50 5		49 52	49 40
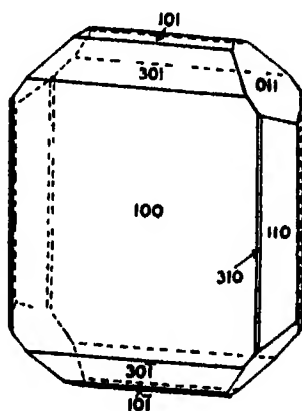
Fig 2 —Ferrous tolueneparasulphonate
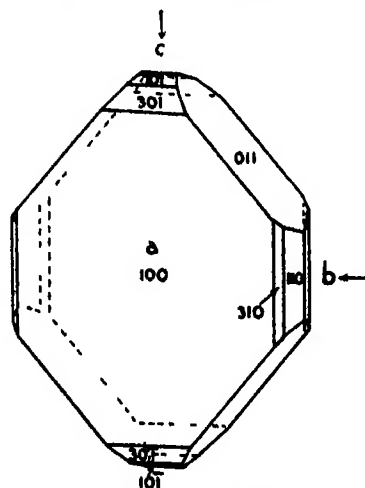
Fig 3 —Cobalt tolueneparasulphonate

Cobalt tolueneparasulphonate, $(C_6H_4 CH_3SO_3)_2Co\ 6H_2O$ —Crystals of this salt are very similar to those of the isomorphous ferrous salt, but the form $q\{011\}$ grows to a greater relative size and the crystals are more massive than those of the ferrous salt (fig 3).

The cleavage is perfect parallel to $a\{100\}$ Twinning on $a\{100\}$

The magnetic behaviour of the salt corresponds with that of cobalt benzenesulphonate.

By far the strongest tendency is for c to set axially.

System : Monosymmetric

$a \cdot b \cdot c = 3\ 9903 : 1 . 1\cdot1080$ $\beta = 88°\ 17'$.

Forms observed · $a\{100\}$, $m\{110\}$, $p\{310\}$, $q\{011\}$, $r\{101\}$, $\rho\{\bar{1}01\}$, $s\{301\}$, and $\sigma\{\bar{3}01\}$

Angle	No of observations	Limits		Mean observed		Calculated	
100 110	32	75°	50'—76° 6'	75°	55¼'	—	
110 Ī10	12	28	1 —28 13	28	8	28°	9'
100 310	1		—	52	59	53	3
011 01Ī	21	83	58 —84 19	84	9½	—	
01Ī 0IĪ	21	95	43 —96 1	95	50½	95	50½
100 011	22	90	55 —91 17	91	0	—	
011 Ī00	21	88	42 —89 2	88	51	88	51
100 ₫01	10	51	10 —51 30	51	20	51	13
Ī00 301	11	49	8 —49 18	49	15	49	12
301 101	5	24	45 —25 4	24	53	24	52
301 Ī01	3	23	35 —23 48	23	39	23	42
101 011	2	49	49 —49 51	49	50	49	48½
011 Ī10	4	43	32 —43 40	43	35	43	33
Ī10 Ī0Ī	1		—	86	36	86	38½

Nickel tolueneparasulphonate, $(C_6H_4CH_3SO_3)_2Ni\,6H_2O$ —This salt crystallises in tablets similar to those formed by the ferrous and cobalt salts   The frequent appearance of the form {210} is to be noticed, this form having been observed only once on crystals of the ferrous salt and not at all on those of the cobalt salt

Cleavage parallel to a\{100\}

The axis b is the direction of greatest magnetic permeability

Vertical axis	Setting	
	Axial	Equatorial
a	b	c
b	a	c
c	b	a

System· Monosymmetric

$a\quad b\quad c = 3\,9949\quad 1 \cdot 1\,1039\quad \beta = 88° 31\frac{1}{2}'$

Forms present $a\{100\}$, $m\{110\}$, $n\{210\}$, $p\{310\}$, $q\{011\}$, $s\{301\}$, $\sigma\{\bar{3}01\}$

Angle	No of observations	Limits		Mean observed	Calculated
100 110	20	75	50′—76° 3′	75° 56½′	—
110 1̄10	6	27	59 — 28 17	28 8	28° 7′
100 210	9	63	11 — 63 28	63 21	63 24
110 210	7	12	26 — 12 34	12 30	12 32½
100 310	1		——	53 13	53 5
011 01̄1̄	19	84	18 — 84 32	84 22	—
01̄1 01̄1̄	19	95	32 — 95 46	95 38	95 38
100 011	17	90	55 — 91 8	90 59½	—
011 1̄00	16	88	56 — 89 5	89 0½	89 0½
100 301	6	51	10 — 51 15	51 12½	51 13
1̄00 301	6	49	23 — 49 30	49 27	49 28½
110 011	1		——	44 23	44 23
1̄10 011	1		——	43 44	43 42

*Magnesium, zinc and manganese tolueneparasulphonates —*In determining the behaviour of these salts a more powerful electromagnet was used than in the case of iron and cobalt salts An improvement in technique was also effected by substituting a thread of cocoon silk for the coarser artificial silk fibre which had sufficed in the earlier experiments, under these conditions, the crystals of the three salts responded readily to the magnetic force All three behaved alike in the following manner —

Vertical axis	Setting	
	Axial	Equatorial
a	*b*	*c*
b	*a*	*c*
c	*b*	*a*

The three salts, therefore, correspond in their magnetic behaviour with the isomorphous nickel salt and with nickel benzenesulphonate.

Salts of benzenesulphonic acids containing halogen in the para-position — The magnesium salts of parachloro-, parabromo- and pariodobenzene-sulphonic acid, crystallising with six molecules of water, measured by Mummery (Part VI, *ante,* p 455), form an isomorphous series with the following salts —

	a	*b*	*c*	*β*
$(C_6H_4.ClSO_3)_2Fe.6H_2O$.	3 6781	1 ·	0·9094	94° 21½′
$(C_6H_4.ClSO_3)_2Co 6H_2O$	3 6603	· 1 .	0·9071	93 46½
$(C_6H_4.BrSO_3)_2Fe 6H_2O$ . .	3·7293	1	0·9104	94 26½
$(C_6H_4.BrSO_3)_2Co.6H_2O$.	3 7103	. 1 :	0 9087	93 59
$(C_6H_4.BrSO_3)_2Ni.6H_2O$	3 7316	: 1 .	0·9139	94 34
$(C_6H_4.ISO_3)_2Fe.6H_2O$	3 7856	· 1 :	0 9085	93 35

The salts of the parachloro-acid are readily soluble in water, those of the bromo-acid are less soluble, the iodosulphonates are but slightly soluble The effect of the halogen in influencing the rate at which the oxidation of a solution of the ferrous salt takes place is particularly striking, whilst a solution of the salt of the chloro-acid blackened in a few days, that of the iodo-acid was scarcely changed after several weeks

Ferrous parachlorobenzenesulphonate, $(C_6H_4ClSO_3)_2Fe\ 6H_2O$ —This salt generally forms tabular crystals, growing on $a\{100\}$, which is the most prominent form The habit is very similar to that of the cobalt salt, which is more fully described

The cleavage is perfect parallel to $a\{100\}$ The magnetic behaviour of the salt is as follows :—

Vertical axis	Setting	
	Axial	Equatorial
a	c	b
b	a	c
c	a	b

The cleavage plane sets in the equatorial plane, unless it be horizontal, exactly as it does in the case of ferrous benzene- and tolueneparasulphonate

System Monosymmetric

$a\ b\ c = 3\ 6781\ 1\ 0\ 9094.\quad \beta = 94° 21\tfrac{1}{2}'$

Forms observed $a\{100\}$, $n\{310\}$, $q\{011\}$, $r\{101\}$, $\rho\{\bar{1}01\}$, and $o\{211\}$
$\rho\{\bar{1}01\}$ is usually poorly developed

Angle	No of observations	Limits		Mean observed	Calculated
100 101	24	71° 55'—72°	10'	72° 2'	—
101 Ī01	16	27 31 —27	55	27 45½	27° 42½'
Ī01 Ī00	14	80 8 —80	17	80 12½	80 15½
011 0Ī1	7	84 19 —84	33	84 27	84 24
0Ī1 0ĪĪ	7	95 29 —95	36	95 33	95 36
100 310	32	50 38 —50	51	50 43	—
310 3Ī0	11	78 31 —78	46	78 35	78 34
101 211	15	39 42 —39	54	39 49	39 48
211 0ĪĪ	9	96 7 —96	23	96 18	96 15
0ĪĪ Ī0Ī	21	43 43 —44	5	43 57	—
100 211	3	67 1 —67	10	67 7	67 3½
211 011	1	——		19 37	19 43½
011 Ī00	2	93 13 —93	14	93 13½	93 13
100 011	2	86 47 —86	48	86 47½	86 47

Cobalt parachlorobenzenesulphonate, $(C_6H_4ClSO_3)_2Co.6H_2O$ —When allowed to crystallise slowly from water, this salt separates in very massive prisms.

The prism zone comprises the forms $a\{100\}$, $\prime\{101\}$, and $\rho\{\bar{1}01\}$, sometimes $\{100\}$ and sometimes $\{101\}$ being most prominent At times, flat plates on $\{100\}$ developed, the habit being then strikingly similar to that of cobalt benzenesulphonate (figs 4 and 5)
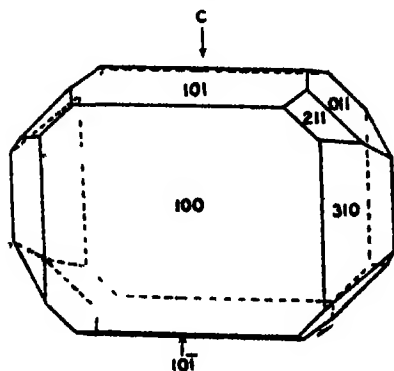
Fig 4

Fig 5

Fig 4 —Cobalt parachlorobenzenesulphonate
Fig 5 —Cobalt parachlorobenzenesulphonate, with axes b and c interchanged to show the resemblance of the crystals to those of the tolueneparasulphonate, fig 2
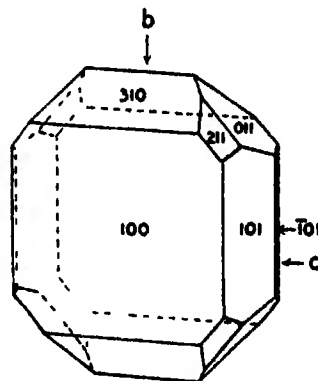
There is a perfect cleavage parallel to $a\{100\}$ on which form twinning sometimes occurs.

The crystals are strongly affected in the magnetic field The strongest tendency is for the axis b to set axially, when b is vertical the tendency to set is noticeably weaker.—

Vertical axis	Setting	
	Axial	Equatorial
a	b	c
b	c	a
c	b	a

System Monosymmetric
$a : b : c = 3{\cdot}6603 : 1 \quad 0\,9071. \quad \beta = 93°\,46\tfrac{1}{2}'$

Forms observed: $a\{100\}$, $n\{310\}$, $m\{110\}$, $q\{011\}$, $r\{101\}$, $\rho\{\bar{1}01\}$, and $o\{211\}$. The form $m\{110\}$ is of rare occurrence

Angle	No of observations	Limits		Mean observed	Calculated
100 101	22	72° 27'—72° 40'		72° 33'	—
101 Ī01	14	27 41—27 52		27 47	27° 47'
Ī01 Ī00	16	79 30 -79 49		79 40	—
011 oĪ1	4	84 18—84 21		84 19	84 18
011 01Ī	5	95 39 -95 43		95 41	95 42
100 310	33	50 24—50 43		50 36	—
310 310	13	78 42—78 50		78 46	78 48
310 110	1	—		24 1	24 5
101 211	2	39 51—39 56		39 53½	39 50½
211:01Ī	2	96 1—96 6		96 3¼	96 4½
01Ī Ī0Ī	2	43 53—43 57		43 55	43 55
100 211	3	67 23—67 25		67 23½	67 22
211 011	4	19 49—19 51		19 50	19 50
011 Ī00	7	92 42—92 49		92 45	92 48
100 011	5	87 12—87 16		87 13½	87 12
101 310	6	79 1—79 4		79 2½	79 2

Ferrous parabromobenzenesulphonate, $(C_6H_4BrSO_3)_2Fe\,6H_2O$ —This salt, although closely isomorphous with the parachlorobenzenesulphonate, differs from the latter in general habit. It forms rhomb-shaped crystals, growing on $r\{101\}$ or $q\{011\}$. The four faces of the form $n\{310\}$ are prominent, forming the sides of the rhomb.

Sometimes the crystals attain to a considerable size but they are then opaque and very fragile

The cleavage is perfect parallel to $a\{100\}$

The magnetic behaviour of the crystals corresponds exactly with that of crystals of the ferrous parachloro-salt.

System · Monosymmetric

$a\ b\ c = 3\,7293\ 1\ 0\,9104\quad \beta = 94°\,26\tfrac{1}{2}'$

Forms observed $a\{100\}$, $r\{101\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, $o\{211\}$, and $\omega\{\bar{2}11\}$.

Angle	No of observations	Limits		Mean observed	Calculated
100 101	18	72° 4' 72° 10'		72° 7½'	—
100 310	29	51 0—51 12		51 6	—
310 110	10	23 47 - 23 55		23 51	23° 51'
101 211	24	39 46—40 2		39 51	—
211 01Ī	24	96 10—96 17		96 13	96 13¼
01Ī Ī0Ī	23	43 52—44 1		43 56	43 55¼
211 110	8	45 34—45 37		45 35	45 35
110 01Ī	3	50 36—50 40		50 39	50 38¼
100 211	6	67 9—67 18		67 12½	67 13
211 011	6	19 28—19 35		19 30¼	19 30
011:Ī00	7	93 12—93 22		93 16	93 17
101 310	10	78 46—78 55		78 51	78 53
100:Ž̄11	1	—		73 18	73 3
Ī01 Ž̄11	1	—		54 11	54 17

Cobalt parabromobenzenesulphonate, $(C_6H_4BrSO_3)_2Co\ 6H_2O$ —In habit this salt resembles the corresponding ferrous salt   Sometimes crystals of a different habit developed, small rhombs growing on $a\{100\}$, the sides of the rhomb being formed by $q\{011\}$, such crystals are similar in habit to those of the benzenesulphonate

Cleavage perfect parallel to $a\{100\}$

The magnetic behaviour of the crystals corresponds with that of cobalt parachlorobenzenesulphonate

System · Monosymmetric

$a\ \ b\ \ c = 3\ 7103\ \ 1\ \ 0\cdot9087\ \ \ \ \beta = 93^\circ\ 59'$

Forms observed $a\{100\}$, $r\{101\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, $o\{211\}$, and, rarely, $\rho\{\bar{1}01\}$ and $\omega\{\bar{2}11\}$

Angle	No of observations	Limits	Mean observed	Calculated
100 101	24	72° 25′—72° 40′	72° 30½′	—
100 310	35	50 58 —51 4	50 58½	—
310 110	13	23 51 —24 1	23 55	23° 54′½
110 110	5	30 7 —30 18	30 14	30 14
101 ; 310	17	79 ′ 1 —79 8	79 4	79 5½
101 211	22	39 48 —40 0	39 54	—
211 110	5	45 31 —45 42	45 36	45 36
110 011	5	50 34 —50 42	50 38	50 35
011 101	23	43 49 —43 58	43 54½	43 55
211 011	19	96 8 —96 17	96 11½	96 11
100 211	7	67 16 —67 35	67 27	67 28
211 011	6	19 31 —19 37	19 35	19 35
011 100	9	92 51 —93 6	92 57	92 57
211 211	2	76 46 —76 50	76 49	76 48
011 011	4	84 16 —84 30	84 25	84 23

Nickel parabromobenzenesulphonate, $(C_6H_4BrSO_3)_2Ni\ 6H_2O$ —The salt forms beautiful, dark-green crystals having the same habit as the ferrous salt. The angular measurements obtained from different crystals were exceptionally constant

The cleavage is perfect parallel to $a\{100\}$. The crystals differ in their magnetic behaviour from both the ferrous and cobalt salts of the same acid.

So long as the axis b is horizontal, it sets in the equatorial position; when b is vertical, an undefined plane lying between the forms $a\{100\}$ and $r\{101\}$ sets in the equatorial plane.

System . Monosymmetric

$a : b \cdot c = 3\cdot7316 . 1 . 0\cdot9139. \ \ \beta = 94^\circ\ 34'$

Forms observed· $a\{100\}$, $r\{101\}$, $s\{301\}$, $n\{310\}$, $q\{011\}$, and $o\{211\}$. $s\{301\}$ is rare.

Angle	No of observations	Limits	Mean observed	Calculated
100 310	26	50° 59'— 51° 15'	51° 7¼'	51° 7'
310 310	14	77 46 — 77 48	77 46½	
100 101	10	71 47 — 72 2	71 54	71 58
100 301	2	50 36 — 50 54	50 45	50 45
101 301	2	21 5 — 21 11	21 8	21 13
101 211	24	39 49 — 39 59	39 55	39 54½
211 011	24	95 59 — 96 7	96 3	96 3¼
011 101	24	43 58 — 44 7	44 2	—
011 011	21	84 38 — 84 41	84 40	—
011 011	21	95 19 — 95 22	95 20	95 20
100 211	2	67 8 — 67 9	67 8½	67 8
211 · 011	2	———	19 30	19 29½
011 100	2	———	93 22	93 22½
100 011	2	86 38 — 86 39	86 38½	86 37½
211 211	3	76 51 — 76 53	76 52	76 52
211 : 211	3	103 7 —103 8	103 7½	103 8

Ferrous pariodobenzenesulphonate, $(C_6H_4ISO_3)_2Fe\,6H_2O$ —This salt crystallises sometimes in rhombic plates, the dominant forms being $a\{100\}$ and $q\{011\}$, more often laminated, opaque crystals growing on $m\{110\}$ or $n\{310\}$ are formed, these are very fragile and unsuited for measurement

The cleavage is perfect parallel to $a\{100\}$

In their magnetic behaviour the crystals correspond with ferrous parachloro- and parabromobenzenesulphonate

System Monosymmetric.

$a . b \cdot c = 3\,7856 \quad 1 . 0\,9085 \quad \beta = 93° 35'$

Forms observed $a\{100\}$, $r\{101\}$, $s\{301\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$, and $o\{211\}$

Angle	No of observations	Limits	Mean observed	Calculated
100 310	24	51° 22'—51° 40'	51° 33'	—
100 110	16	75 2 —75 23	75 12½	75° 10½'
310 110	14	23 32 —23 48	23 38	23 37½
110 110	6	29 30 —29 48	29 36	29 39
100 : 301	3	51 49 —51 57	51 53	51 54
100 101	3	73 1 —73 17	73 8	73 8½
301 101	3	21 4 —21 30	21 12	21 14½
011 011	16	84 20 —84 28	84 24	—
011 011	17	95 35 —95 40	95 37	95 36
100 211	7	68 0 —68 18	68 6	68 5
211 011	7	19 12 —19 18	19 15½	19 15½
100 011	22	87 12 —87 33	87 20½	—
011 100	21	92 29 —92 47	92 39	92 39½
101 011	3	43 49 —43 59	43 53	43 52

Cobalt   pariodobenzenesulphonate, $(C_6H_4ISO_3)_2Co.6H_2O$.—We have not succeeded in growing crystals of this salt suitable for accurate measurement;

the crystals we have obtained proved to be isomorphous with the corresponding ferrous salt

The cleavage is perfect parallel to $a\{100\}$.

In their magnetic behaviour the crystals correspond with those of cobalt parachloro- and parabromobenzenesulphonate

Paradichlorobenzenesulphonates —Magnesium and zinc paradichlorobenzene-sulphonates were described in Part IV and the following axial ratios were there assigned to them.

	a	b	c	β
$(C_6H_3Cl_2SO_3)_2Mg\,8H_2O$ ..	2 4539	1	2 9985	79° 20'
$(C_6H_3Cl_2SO_3)_2Zn\,8H_2O$.	2 4450	1	2 9970	79 14$\frac{1}{2}$

The ferrous and cobaltous salts are closely isomorphous with the magnesium and zinc salts. When either of the salts is suspended in the magnetic field with the b axis vertical, the crystal sets with the face $\{101\}$ in the equatorial plane in the case of the former, in the axial plane in that of the latter. Further examination of the crystals, suggested by this last observation, revealed the fact that $r\{101\}$ is a plane of cleavage, a fact which had been overlooked in the case of the zinc and magnesium salts. From these observations it would appear that the plane $\{101\}$, being so important a plane in the crystal structure, should be chosen as the pinacoid $a\{100\}$, it would then correspond with the $\{100\}$ plane of the benzene-, toluene- and parahalogenbenzene-sulphonates both in being a cleavage plane and in setting equatorially in the ferrous and axially in the cobalt salt. The change suggested involves a change of the interaxial angle β, $\{101\}$ becoming $\{100\}$ and $\{001\}$ becoming the new $\{101\}$. The axial ratios of the four salts, determined from the new setting, are as follows :—

	a	b	c	β
$(C_6H_3Cl_2SO_3)_2Mg.8H_2O$	1·7562	1	2 0960	78° 13$\frac{1}{2}$'
$(C_6H_3Cl_2SO_3)_2Zn.8H_2O$	1 7528 . 1		2 1055	78 24
$(C_6H_3Cl_2SO_3)_2Fe\,8H_2O$ ..	1 7543 : 1 .		2 1053	78 40
$(C_6H_3Cl_2SO_3)_2Co\,8H_2O$ ..	1 7456	1	2 1034	78 15$\frac{1}{2}$

Ferrous paradichlorobenzenesulphonate, $(C_6H_3Cl_2SO_3)_2Fe\,8H_2O$ — Good crystals of this salt were obtained by allowing a saturated solution to evaporate very slowly. They were well developed, short, stout prisms, the prism axis being the axis of symmetry. The two ends of the prism are differently developed, the hemimorphic character of the crystals being clearly shown. Generally the form $\{110\}$ appeared at both ends : at one end this was accompanied by $\{011\}$ and $\{111\}$, at the other by $\{0\bar{1}2\}$. Sometimes $\{1\bar{1}1\}$ appeared also.

When a crystal is suspended in the magnetic field, so long as the axis b is

horizontal, this axis sets equatorially with great force. When b is vertical, the face $a\{100\}$ sets strongly in the equatorial plane. The axis c is then at right angles to the lines of force but the axis a is not parallel to them but inclined at an angle of $11° 20'$ because β is not a right angle but has the value $78° 40'$

System Monosymmetric hemimorphic

$a \quad b \quad c = 1\cdot7543 \quad 1\cdot2\cdot1053 \quad \beta = 78° 40'$

Forms observed $a\{100\}$, $m\{110\}$ and $\{1\bar{1}0\}$, $q\{011\}$, $p\{0\bar{1}2\}$, $\iota\{001\}$, $r\{101\}$, $\rho\{10\bar{1}\}$, $d\{102\}$, $o\{111\}$ and $\{1\bar{1}1\}$.

Angle	No of observations	Limits	Mean observed	Calculated
100 110	25	59° 40'—60° 6'	59° 50'	—
110 $\bar{1}$10	9	60 16 —60 25	60 20	60° 20'
110 101	23	68 48 —69 8	68 56	—
101 011	9	75 59 —76 33	76 14	76 16
011 $\bar{1}$10	7	34 31 —35 3	34 49	34 48
001 110	23	95 29 —95 49	95 40	—
110 111	13	21 27 —22 5	21 49	21 48
111 00$\bar{1}$	13	62 24 —62 33	62 29	62 32
110 00$\bar{1}$	18	84 14 —84 31	84 20	84 20
100 101	15	43 59 —44 40	44 19	44 20
101 102	2	23 21 —23 28	23 24½	23 18
102 00$\bar{1}$	2	33 36 —33 45	33 40½	33 42
101 001	10	56 57 —57 7	57 1	57 0
001 $\bar{1}$01	9	43 23 —43 49	43 34	43 36
$\bar{1}$01 $\bar{1}$00	8	34 51 —35 8	35 3	35 4
001 $\bar{1}$00	11	78 23 —78 52	78 43½	78 40
001 011	10	63 56 —64 21	64 8	64 9
001 0$\bar{1}$2	10	45 51 —45 57	45 53	45 54

Cobalt para dichlorobenzenesulphonate, $(C_6H_3Cl_2SO_3)_2Co\,8H_2O$—When it separates rapidly, this salt forms groups of long thin prisms but if crystallisation be allowed to proceed slowly, well-developed short prisms belonging to the hemimorphic class of the monosymmetric system are formed These are similar to those of the ferrous salt, the forms developed being the same.

The cleavage is perfect parallel to $a\{100\}$

Magnetically the crystals behave in a manner exactly opposite to that of the ferrous salt The axis b, when the crystal is suspended with this axis horizontal, sets axially when b is suspended vertically, the face $a\{100\}$ sets in the axial plane

System Monosymmetric hemimorphic.

$a \quad b \quad c = 1\cdot7456 \quad 1\cdot2\cdot1034. \quad \beta = 78° 15\frac{1}{2}'$

Angle	No of observations	Limits	Mean observed	Calculated
100 110	26	59° 37′—59° 42′	59° 40′	—
110 1̄10	11	60 37 —60 44	60 40	60° 40′
101 111	19	76 14 —76 30	76 23	—
011 1̄10	17	34 34 —34 55	34 47	34 47
1̄10 10̄1	23	68 43 —68 58	68 50	—
100 101	14	44 11 —44 29	44 23	44 21½
101 : 102	13	23 17 —23 30	23 25	23 28
102 001	9	33 52 —34 4	33 57	33 55
001 1̄01	5	43 27 —43 34	43 30	43 27
1̄01 1̄00	9	34 36 —34 55	34 47	34 48½
1̄01 1̄11	10	50 7 —50 16	50 13	50 13
101 01̄2	8	67 51 —68 6	67 59	67 57
01̄2 1̄11	8	28 51 —29 5	28 56	28 58
1̄11 10̄1	9	83 2 —83 11	83 6	83 5
1̄01 011	2	71 32 —71 33	71 32½	71 31
011 110	3	42 53 —43 0	42 57	42 59
110 10̄1	2	——	65 32	65 30

Significance of the Magnetic Behaviour of Salts

The observations now recorded of the magnetic behaviour of the salts examined are of special interest in that we have found that salts of ferrous iron and of dyad cobalt are very sensitive to magnetic influence, whilst those of nickel are but feebly affected and those of manganese only respond when the field is a very strong one, no more readily than do those of magnesium and zinc. On the other hand, copper salts are about as sensitive as those of nickel The readiness of response is to be correlated perhaps rather with the appearance of colour than with the presence of a magnetic metal in the salt

The opposite behaviour of iron and cobalt in structures which presumably only differ in having the one or the other metallic atom at the centre of the molecular system is very remarkable.

But it is clear that the constitution of the salt plays an important part in such phenomena. Whilst the yellow salt potassium ferrocyanide is not in the least disturbed in the field of our weaker magnet, the red ferri-cyanide is powerfully affected. Strange to say, the very pale yellow salt, potassium cobalticyanide, is unaffected even in the field of our stronger magnet; several platinocyanides we have tested are also unaffected. Preliminary observations we have made with several of the pseudotrigonal salts of rare-earth metals (Nd, Pr, Gd) described in Part III show that these are more or less powerfully directed.

It is obvious that a wide field for study has been opened up. We propose to prosecute the inquiry in various directions and to ascertain

whether magnetic susceptibility is in any way to be correlated with the appearance either of colour or of an unsaturated condition, particularly as this latter is known to influence optical refractive power in a high degree

The special influence exercised by iron and cobalt is the more remarkable in view of the agreement in behaviour of salts of copper, nickel, manganese, zinc and magnesium   The behaviour of salts of other metals remains to be determined and will be made the subject of systematic study, to ascertain whether or not iron and cobalt stand alone

As non-isomorphous but morphotropically related salts of a metal have similar magnetic properties in corresponding directions, the magnetic behaviour of crystals may prove to be of great value as a means of discovering relationships in crystalline structure in cases in which these are not immediately obvious—several such cases are discussed by us Similarly, it is to be anticipated that the magnetic behaviour will be of use, in doubtful cases, in arriving at a correct mode of setting a crystal.   In orthorhombic crystals, the directions which set either axially or equatorially appear always to correspond with a crystallographic axis, it will be rational, therefore, in the case of monosymmetric crystals, to apply this principle in selecting axial directions.

The Marshalling of Benzene Units in Sulphonates

In Part V of these studies, we have advanced a very considerable body of evidence that the parameter which presumably is the measure of the thickness of the individual layers of the benzenoid molecules in a crystal has a value very slightly removed from that which it has in benzene itself when the marshalling is hexagonal, viz 2·78   In the second form of marshalling foreseen by Barlow and Pope,[*] which has rhombohedral symmetry, the layers are supposed to be of less thickness and they have suggested that this form is met with in paradiiodobenzene and a number of similar compounds   In the third of these studies, on account of the pseudo-trigonal character of various sulphonates of rare earth metals and the very close resemblance they bear to paradiiodobenzene, we were led to assume that in most of the salts examined the low value of the z parameter was evidence of rhombohedral marshalling of the benzene units.   This conclusion was extended to salts of dyad and of some monad metals in Part IV (p. 308) · the silver salt alone appeared to be an exception.

The results recorded in Part V have led us to think, however, that the z' (and correlatively the y) dimension may be subject to not inconsiderable fluctuation without an alteration in the marshalling.   In the case of the salts

* Cf Part V, p. 115, figs. 4 and 5

considered, if the benzene residues are separated in the manner we have suggested to a considerable extent by intervening "blocks" of water of crystallisation, it is to be expected, we should imagine, that these "blocks" would be piled perpendicularly rather than diagonally and would therefore tend to prevent the shear from taking place that is involved in the passage from hexagonal to *rhombohedral symmetry*

On the whole, we are inclined to think that the evidence generally favours the view that the dimensions are subject to more or less variation but that the general mode of arrangement remains the same Bridgman's recent discovery of a second crystalline form of benzene, stable only under pressure, is not without significance perhaps from this point of view, it may well be the second form adumbrated by Barlow and Pope In any case, the question we raise is one of importance to be considered carefully as opportunity offers.

The Influence and Distribution of Water of Crystallisation

The salts we have studied have other peculiarities, however, which render them of special interest.

The close relationship between corresponding benzenesulphonates and toluenesulphonates has been pointed out already in Part IV (p 307) The relationship is sufficiently apparent on inspection of the axial ratios, whilst the introduction of CH_3 in the para position has no effect on the ratio b c, it involves a considerable alteration of the ratio a b. It is therefore clear that, as in the cases discussed in Part V, an extension takes place only in one direction, when the equivalence parameters are calculated, it appears that the alteration is precisely in the proportion of the alteration of the valency volume from 100 to 112

But the axial ratios of the substituted benzenesulphonates containing a single atom of halogen are in no apparent relationship with those of the benzenesulphonates, thus

		a	b	c	β
I.	$(C_6H_5SO_3)_2Fe\ 6H_2O$	3 5690 · 1 ·	1·1058		86° 18'
II	$(C_6H_4CH_3SO_3)_2Fe.6H_2O$.	3 9972 1 .	1 1051		88 37
III.	$(C_6H_4ClSO_3)_2Fe\ 6H_2O$.	3 6781 · 1 :	0 9094		94 21½

On comparing the magnetic properties of the three salts, however, it appears that, whilst I and II can both be represented by the scheme $a > b > c$, that representing III is $a > c > b$. If now the assumption be made that the directions in crystals which correspond magnetically also correspond geometrically, it is plain that, in order to make III correspond with I and II,

it is necessary to interchange b and c in the case of this substance   The axial ratios then become :—

	a	b	c	
$(C_6H_5SO_3)_2Fe\ 6H_2O$	3 5690	1	1 1058	$\beta = 86° 18'$
$(C_6H_4CH_3SO_3)_2\ Fe\ 6H_2O$.	3 9972 : 1		1·1051	$\beta = 88\ 37$
$(C_6H_4ClSO_3)_2Fe\ 6H_2O$	4 0445	1	1 0996	$\gamma = 94\ 21\frac{1}{2}$

In the case of all three salts the ratio c b is practically constant   Moreover, when the crystals are regarded from this point of view, the correspondence is complete between all three with regard to habit, to forms developed and to cleavage, as well as in magnetic behaviour (cf figs 4 and 5)

It is certainly remarkable that the axial ratio $a \cdot b$ of the parachloro-salt is practically the same as that of the toluenesulphonate   The valency volume of chlorine being unity, a close correspondence is to be expected between the benzenesulphonate and the parachloro-derivative* and, as a matter of fact, it is shown in the previous communication by Mummery (p 455) that the sulphochlorides $C_6H_4Cl\ SO_2Cl$, $C_6H_4Br\ SO_2Cl$ and $C_6H_4I.SO_2Cl$ have equivalence parameters in accordance with this assumption   It might be argued from this, as the chlorine atom produces the same effect on the ratio a b as the methyl group, that Cl and CH_3, not Cl and H, occupy the same volume That such a conclusion would be, to say the least, a rash one, however, the following argument will show

To admit that Cl and CH_3 have the same volume would be to return to the view held by Kopp and it would then follow that Br has an atomic volume much greater than that of either, iodine a still greater volume   Kopp's values are $CH_3 = 27·5$, $Cl = 22\ 7$, $Br = 53\ 4$ Accepting these, bromine should produce a change more than twice as great as that produced by chlorine , iodine would produce a still greater change

The measurements of the three sulphochlorides made by Mummery, referred to above, afford no support to this view, moreover, in the case of the sulphonates, chlorine, bromine and iodine produce much about the same effect on the ratio $a : b$, the slight rise as the atomic weight increases agreeing with the slight increase of the size of the sphere of influence of the halogen atom, in passing from chlorine to iodine, suggested by Barlow and Pope

	a	b	c	
$(C_6H_5SO_3)_2Fe\ 6H_2O$	3 5690	1	1 1058	$\beta = 86° 18'$
$(C_6H_4ClSO_3)_2Fe\ 6H_2O$ ...	4 0445	1 ·	1 0996	$\gamma = 94\ 21\frac{1}{2}$
$(C_6H_4BrSO_3)_2Fe\ 6H_2O$.	4 0964	1	1·0984	$\gamma = 94\ 26\frac{1}{2}$
$(C_6H_4ISO_3)_2Fe\ 6H_2O$	4·1670	1	1 1007	$\gamma = 93\ 35$

* Cf Part V, Table I, p. 121.

It must therefore be admitted that the three halogens have practically the same valency volume   It is still necessary, however, to account for the effect on the crystal structure of the benzenesulphonate of the substitution of hydrogen by halogen   It will be observed that in each salt (I, II and III) in the first table in this section, the monosymmetric angle β is not far removed from a right angle , in fact the departure from orthorhombic symmetry involves only a slight shear   In the case of I and II, this shear has taken place in one and the same direction in the structure , in the case of III it is in a direction at right angles to that in which it has taken place in II and III   hence when III is made comparable with I and II, by interchanging the axes b and c, the interaxial angle becomes γ instead of β It is suggested that the peculiarity in the halogen atom which brings about this change, whether it be owing to a slight increase of its sphere of influence over that of the hydrogen atom displaced or whether it be due to the introduction of a new centre of influence, produces some slight readjustment of the constituent units in the structure   That the modification of internal structure is a very slight one follows from the general similarity of habit found to exist between the ferrous benzenesulphonate and the parachlorobenzenesulphonate.   The nett result of the substitution of hydrogen by halogen is to change slightly the shape of the parallelepipedal cell or space lattice, elongating it in one direction and shortening it in the same proportion in the other two, so that the ratio c b remains unchanged

But the increase in the one direction, which brings the substituted benzenesulphonates into apparent harmony with the toluenesulphonates,* is so considerable that it is not improbable that a special influence is at work in the case of the former salts and that they are in some respects different in constitution from the benzene- and toluenesulphonates.   The still greater departure of the dichlorosulphonates, obvious in the fact that these contain a larger proportion of water of crystallisation ($8H_2O$ instead of $6H_2O$), is not without importance from this point of view.   It must not be forgotten that the acids free from halogen differ to a not inconsiderable extent in properties from the substituted acids . the difference is particularly obvious perhaps in the case of the corresponding anhydrides· thus, whereas benzenesulphonic anhydride is described as deliquescent and easily soluble in water, which hydrolyses it readily, the anhydride of the paradibromo-benzenesulphonic acid is insoluble in most solvents and is hydrolysed with difficulty.

Such differences are indications that the forces operative within the molecules are very different . presumably, the " sulphonic region " is the

* Not improbably the coincidence is accidental.

one specially affected and as the " water " is present in this region it is probably subject to these special influences   The results obtained by Tamman and by Bridgman in recent years are proof that water may undergo great changes in volume and it can scarcely be doubted that the changes in volume are the consequences of alteration in the structure of the complex perhaps more or less of the character pictured by one of us in discussing the nature of water *

It is commonly assumed that, in the case of salts of multivalent metals, the acid radicles are in direct association with the metallic atom, which serves as the link , the so-called water of crystallisation is pictured, as a rule, as an addition to the complex.   Our view practically involves the assumption that the metallic atom is at the centre of the system, as space cannot well be found for the water molecules if the metal serve as the direct link   If the views applied by Armstrong and Worley to sulphuric acid† are applied generally to salts containing water of crystallisation, there is no difficulty in picturing the several molecules of "hydrone" taking up the position of intermediaries and the metallic atom—probably in the form of metallic oxide —as placed in whatever position its own influence and that of the acidic groups may reciprocally determine   From this point of view, *the form of water* present in a salt may vary according to the influences at work

It is assumed by Barlow and Pope that when a variation in volume takes place, the volumes of the different atoms in a molecule vary concomitantly, so that they remain relatively the same , in other words, the valency-volume is a constant

It appears to us that, in special cases such as we are considering, in which a molecule is built up of several systems each of which is deformable within certain limits, the one complex may be more or less deformable independently of the other

The equivalence parameters of the salts under consideration, calculated from the axial ratios without modification, are as follows —

* 'Roy Soc Proc,' A, vol. 81, p 80 (1908).
† *Ibid.*, vol. 90, p. 73 (1914)

	x	y	z	W
$(C_6H_5 \cdot SO_3)_2$ Fe $6H_2O$	10 4900	3 2502	2·9391	100
,, Co ,,	10 4560	3 2599	2 9405	100
,, Ni ,,	10 4430	3 2604	2·9437	100
$(CH_3 \cdot C_6H_4 \cdot SO_3)_2$ Fe $6H_2O$	11·7440	3·2469	2 9881	112
, Co ,,	11 7210	3 2546	2·9374	112
,, Ni ,,	11 7440	3 2452	2·9397	112
$(Cl \cdot C_6H_4 \cdot SO_3)_2$ Fe $6H_2O$	11 4260	3 1066	2 8251	100
,, Co ,,	11 3960	3 1136	2 8244	100
$(Br \cdot C_6H_4 \cdot SO_3)_2$ Fe $6H_2O$	11 5290	3 0914	2 8144	100
,, Co ,,	11 4940	3·0980	2 8151	100
,, Ni ,,	11 5195	3·0870	2 8212	100
$(I \cdot C_6H_4 \cdot SO_3)_2$ Fe $6H_2O$	11 6395	3·0747	2 7933	100

The y and z values thus found appear to us to be more in accordance with those deduced as characteristic of a great variety of benzene derivatives in Part V of these studies than are those calculated from modified values of the axial ratios in Part IV Though the z values are relatively high, those of y are correspondingly low, but the great increase of x, in the case of the substituted benzenesulphonates, appears to need some special explanation such as we now venture to put forward

[*Note added June* 22 —We have recently obtained a crystal of ferrous benzenesulphonate—a strongly paramagnetic substance—(similar in shape to fig. 3) the dimensions of which in the direction of its three axes, a, b, and c, are 1/16″, 1/2″ and 1″ respectively When suspended with the axis b vertical, this crystal is powerfully directed so that the a axis sets along the lines of force, though its length in the direction of the c axis— which sets at right angles to the lines of force—is 16 times as great as is the length in the direction of a

A crystal of the corresponding paramagnetic cobalt salt of similar shape sets with the c axis along the lines of force. The behaviour of the iron salt, coupled with the difference between the two salts, is at once a proof that the property we have brought under notice is a function of the internal structure of the crystal and not that of a merely paramagnetic substance.

Moreover, if the dimensions of the crystal in the direction of the different

axes be entirely changed by cutting sections, the setting of the mass with respect to the axes of the crystal remains unaltered   This is true of all the crystals we have examined, whether paramagnetic or diamagnetic

In view of the known connexion between optical and magnetic phenomena, the possibility that coloured substances might be specially affected in a magnetic field led us to examine the behaviour of crystals of azobenzene, a brilliantly orange-red coloured substance

Azobenzene is monosymmetric, its axial ratios being

$$a \ b \ c = 2\ 1076 \ 1 \ 1\ 3312 \quad \beta = 65° \ 34' *$$

A form $\{\bar{4}01\}$, not recorded by Boeris, is also sometimes apparent   If the form $\{\bar{4}01\}$ be changed to $a\{100\}$, $c\{001\}$ remaining the same, $\{100\}$ becoming $\{101\}$, the axial ratios are

$$a \ b \ c = 2\ 1076 \ 1 \ 4\ 8492 \quad \beta = 91° \ 7'$$

This alteration involves a simplification of the indices, as $\{201\}$ becomes $\{101\}$, $\{\bar{4}03\}$ $\{\bar{2}03\}$ and $\{021\}$ $\{011\}$

The valency volume W is 64   if b be doubled, the equivalence parameters when b and c are interchanged are

$$x \ y \ z = 3\ 0837 \ 7\ 0946 \ 2\ 9261$$

The x and z parameters thus deduced are very similar to those of benzene, whilst y is slightly more than double the corresponding benzene parameter.

Crystals of azobenzene are affected quite strongly in a magnetic field, even in that of our smaller magnet   The direction of greatest permeability lies along the axis of symmetry b this axis always tends to set along the lines of force   This direction corresponds to that of the z parameter, i e, to the direction in which we suppose the benzene units to be stacked   It is in this direction also that the doubly linked nitrogen atoms would be in greatest proximity to one another   When the crystals are suspended so that this direction is vertical, the direction of the x parameter (the a axis) sets axially, and it is in this direction presumably that the colour-producing centres are closer together than in the direction perpendicular thereto

In view of the striking crystallographic similarity between the salts of tolueneparasulphonic and parachlorobenzenesulphonic acid containing dyad metals, it is obviously important to study the salts which these acids form with monad metals.   We have examined crystals of the anhydrous potassium salt of parachlorobenzenesulphonic acid   Measurements of a potassium chlorobenzenesulphonate are recorded by Boeris·† he does not

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* Boeris, 'Zeit für Kryst,' vol. 34, p 301 (1901)
† 'Zeit für Kryst,' vol. 20, p 526

say that his was the para-salt but the exact agreement between his data and ours proves that it must have been

The salt crystallises from water in well formed rhombs or prisms, the habit being variable Generally $q\{011\}$ and $m\{110\}$ are prominent and in the rhombs $r\{\bar{1}01\}$ is large, $c\{001\}$ appearing as a narrow face The cleavage is perfect parallel to $a\{100\}$. The plane of $a\{100\}$, however, rarely develops as a face

Forms observed $a\{100\}$, $c\{001\}$, $r\{\bar{1}01\}$, $m\{110\}$, $n\{120\}$, and $q\{011\}$.

System Monosymmetric

$a \quad b \quad c = 1\,4394 \quad 1 \quad 0\,9049 \quad \beta = 97° \, 11'$.

(Boeris gives $1\,4379 \quad 1 \quad 0\,9045 \quad \beta = 97° \, 16'$)

Angle	No of observations	Limits		Mean observed	Calculated	Boeris
$\bar{1}01$ 011	21	51° 52'—52°	2'	51° 58'	—	51° 58'
011 110	21	52 55 — 53	9	53 5	—	53 4
110 10$\bar{1}$	19	74 50 — 75	1	74 56	74° 57'	74 58
011 0$\bar{1}$1	14	83 48 — 83	52	83 50	—	83 48
011 001	12	41 53 — 41	58	41 55	41 55	41 54
011 01$\bar{1}$	14	96 7 — 96	14	96 10	96 10	96 12
$\bar{1}$00 $\bar{1}$01	3	62 59 — 63	3	63 2	63 5	—
$\bar{1}$01 001	4	34 6 — 34	12	34 8	34 6	—
100 110	4	54 52 — 55	8	55 0	55 0	54 58
110 120	8	15 36 — 15	55	15 47	15 42	—
120 ; $\bar{1}$20	4	38 21 — 38	47	38 34	38 36	—
100 120	3	70 42 — 70	48	70 45	70 42	—
011 $\bar{1}$20	1	————		53 10	53 9	53 12
011 120	3	48 35 — 48	40	48 37	48 36	48 36

When the constants of this anhydrous salt are compared with those of the corresponding hydrated cobalt salt, interesting resemblances are revealed —

	a	b	c	β	Cleavage
Cl⟨⟩SO₃K	1 4394	1	0 9049	97° 11'	$a\{100\}$
(Cl⟨⟩SO₃)₂Co 6H₂O	3 6603	1 :	0 9071	98 46½	$a\{100\}$

The ratio $c \cdot b$ is practically the same in the case of each salt the cleavage is also in the same direction ; the ratio $a \cdot b$, however, is much greater in the case of the hydrated cobalt salt From these facts, it is obvious that the two salts are structurally similar, when the equivalence parameters are contrasted, an even more striking relationship becomes apparent.

	W	x	y	z
Cl⟨ ⟩SO₃K	38	4 4428	3 0865	2 7930
(Cl⟨ ⟩SO₃)₂Co 6H₂O	100	11 3960	3 1136	2 8244

The y and z parameters of the two salts are practically equal   it is as if in the cobalt salt the two component units (Cl⟨ ⟩SO₃) were joined by the metallic atom, and that the water molecules are enclosed between them in the manner suggested in Part IV of these Studies (p 310)   The relationship between the potassium and cobalt salts cannot well be accounted for in any other manner]

Dimethylenediol Peroxide (Diformal Peroxide Hydrate).

By H. J. H. Fenton, M.A., Sc D , F R S

(Received and read May 28, 1914)

The conditions of the co-existence of hydrogen dioxide and formaldehyde, and the nature of their interaction, are of special interest in connection with the theories which have been advanced to account for the photosynthesis of carbohydrates in plants

As the initial stage in the assimilation of carbon dioxide, Bach[*] suggested that carbon dioxide in presence of water gives rise to percarbonic acid (H_2CO_4) and formaldehyde, whereas Usher and Priestley[†] consider that the primary products are hydrogen dioxide and formaldehyde, the change being reversible in the sense

$$CO_2 + 3H_2O \rightleftharpoons H CHO + 2H_2O_2$$
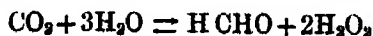
This view has been opposed by various authors, one ground for objection being the, presumably, incompatible nature of the two compounds named.

The interaction of hydrogen dioxide and formaldehyde was first studied by Blank and Finkenbeiner,[‡] who showed that, in presence of alkalis,

[*] 'Comptes Rendus,' vol 116, p 1145 (1893)
[†] 'Roy Soc Proc,' vol. 77, p. 369 ; vol 78, p 318 (1906) , and vol 84, p. 101 (1911).
[‡] 'Ber ,' vol 31, p 2979 (1898).

hydrogen is evolved and that the change may be employed for the quantitative estimation of formaldehyde   They represent the change as

$$2H CHO + H_2O_2 + 2NaOH = 2H.COONa + 2H_2O + H_2.$$
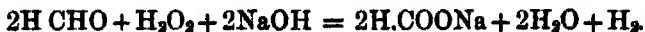
Geisow* afterwards studied the action in neutral or acid solution when warmed in a water-bath and he states that, under these conditions, the products are carbon dioxide and hydrogen, no formic acid being produced,

$$H CHO + H_2O_2 = CO_2 + H_2O + H_2.$$

Since barium dioxide behaves similarly to hydrogen dioxide, it would appear that the hydrogen evolved is derived from the formaldehyde

Lyford,† on the other hand, finds that formic acid is produced as the initial stage,

$$2H CHO + H_2O_2 = 2H COOH + H_2,$$
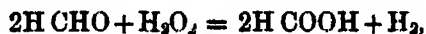
and is subsequently oxidised to carbon dioxide and water

In the course of some experiments bearing on these questions, it has been observed that when a strong solution of formaldehyde (*e g*, commercial formalin) is mixed with pure 100-volume hydrogen dioxide (Merck's perhydrol) in about equal volumes, and the mixture is allowed to evaporate at a low temperature, in a vacuum desiccator over sulphuric acid, a brilliant crystalline mass is obtained, consisting of large, transparent, rectangular plates or prisms   The exact proportions of the reagents employed do not greatly matter, if, however, the formaldehyde is in large excess, the soft colloidal polymer of formaldehyde separates, and, if the dioxide is in excess, the crystallisation is retarded or prevented.   The crystals are odourless, but they emit a strong ozone-like odour when treated with sulphuric acid

This crystalline compound has interesting properties, it melts at about 65°, and, if heated a few degrees above this temperature, it explodes with detonation, the products having a strong odour of formaldehyde. If the powdered substance is brought into contact with reduced iron (*ferrum redactum*) or platinum black, it immediately bursts into flame, and with cupric oxide it behaves similarly when gently warmed. Mixed with inert powders, such as silica, it decomposes suddenly on warming, but without explosion or ignition.

The substance dissolves very easily in water, alcohol, or acetic acid, and sparingly in anhydrous ether, from the latter solvent it may be recrystallised unchanged.   The aqueous solution is neutral, and, as will be seen below, is remarkably stable at a low temperature.   On addition of alkalis, hydrogen

* 'Ber ,' vol 37, p 515 (1904)
† 'Journ. Amer. Chem. Soc ,' vol. 29, p. 1227 (1907).

is immediately evolved. The freshly prepared solution gives, at first, only the faintest possible yellow colour with titanic acid, but the colour slowly develops on standing With chromic acid and ether, the indication of hydrogen dioxide is very slight, and with potassium iodide, in presence of dilute sulphuric acid, iodine is only very slowly and incompletely liberated. Rimini's phenylhydrazine and nitroprusside reagent gives only a feeble indication of formaldehyde, and Schiff's magenta reagent gives an entirely negative result   If, however, the aqueous solution is mixed with a little platinum black, a rapid catalytic decomposition ensues ; the resulting solution has then a strong odour of formaldehyde and gives all the reactions of this substance with intensity

The analysis of the compound by combustion presented, as might be expected, exceptional difficulties owing to its explosive character and its behaviour when warmed with cupric oxide or with inert powders   Eventually, however, the combustion was successfully carried out by keeping the substance in the combustion tube at a temperature only just above its melting point, by means of a carefully regulated current of hot air, for about 20 to 30 minutes. Under these conditions, decomposition takes place with evolution of gas but without explosion, and the temperature is only allowed to rise when the liquid has all disappeared ; a piece of platinum wire placed in the boat suitably accelerates the decomposition   For analysis, the substance was recrystallised from anhydrous ether and kept in a vacuum desiccator

$$0\ 1770\ \text{substance gave } 0\ 1696\ CO_2 \text{ and } 0\ 1015\ H_2O$$

$$C = 26\ 13,\ H = 6\ 36\ \text{per cent}$$

The formula $2H\ CHO\ H_2O_2$ requires—C, 25 55 ; H, 6·38 per cent

Confirmation of this formula was afforded by gasometric determination of the hydrogen evolved by the action of alkalis. It will be observed that the relation of the constituents is that required by the equation of Blank and Finkenbeiner quoted above.

I. 0 1628 grm substance treated with 25 c c of 2N KOH gave 36·5 c.c. of hydrogen (corr.)   Theory requires 38 7 c c

II 0·0697 grm substance gave 15 9 c c of hydrogen (corr)   Theory requires 16 6 c.c

The results were just the same if an excess of hydrogen dioxide was previously added

From these results there is every probability that the compound is identical with that which Legler obtained, in 1881, by the slow oxidation of ether in contact with slightly glowing platinum foil.[*] The products of this

* 'Ber,' vol. 14, p 602 (1881), and vol 18, p. 3343 (1885).

1

Magnet on

2

Magnet off

Photos 1 and 2 — Explosion-wave in Mixture $CN_2 + O + N$

3

Magnet on

4

Magnet off

Photos 3 and 4 — Explosion-wave in Electrolytic Gas

5

Magnet on

6

Magnet off

PHOTOS 5 AND 6   Explosion-wave in Mixture $C_2H_2+5O_2$

7

Magnet on
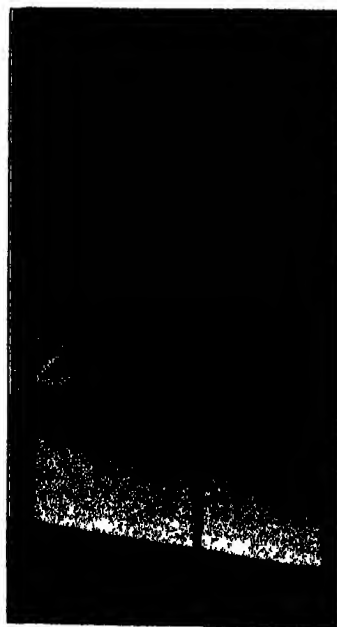
8

Magnet off

PHOTOS 7 AND 8   Explosion wave in Mixture CS_2+3O_2
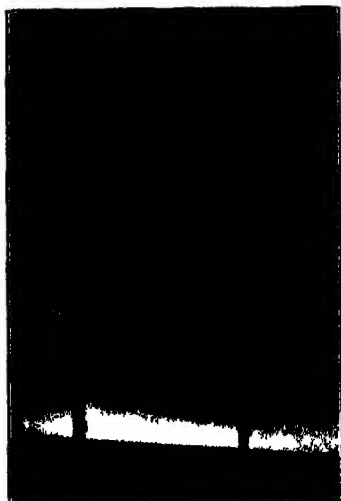
9
Magnet on
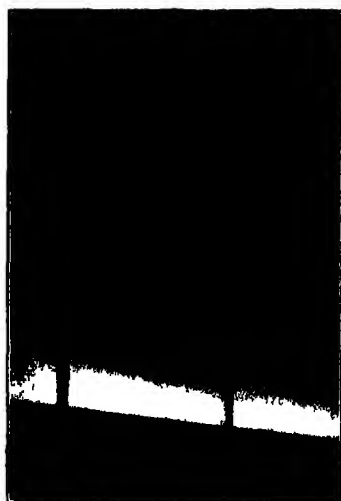
10
Magnet off

Photos 9 and 10 —Explosion-wave in Mixture $2CO + O_2$

11
Moist —Magnet on
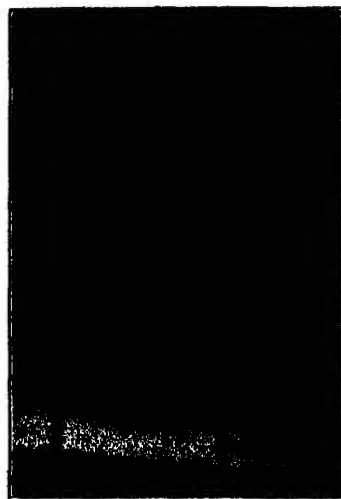
12
Dry - Magnet on

Photos 11 and 12 —Explosion wave in Moist and Dry Mixture $2CO + O_2$

13

Magnet on

14

Magnet off

PHOTOS 13 AND 14   Spark passed outside Poles in Mixture $C_2H_2+5O_2$

15

Magnet on
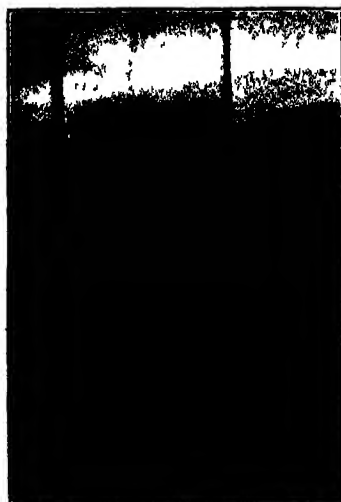
16

Magnet off

PHOTOS 15 AND 16 —Spark passed in Centre of Field in Mixture $C_2H_2+5O_2$

reaction were found to be acetaldehyde, acetic acid, formic acid, formaldehyde, hydrogen dioxide, and a crystalline compound to which the author first assigned the formula $C_{11}H_{22}O_{21}$. Later, however, from measurement of its decomposition products, he concluded that the formula was $(CH_2O)_6 O_4 + 3H_2O$, and he called it hexahydroxymethylene peroxide

Nef[*] afterwards obtained a direct compound of hydrogen dioxide and benzaldehyde, to which he assigned the formula $O_2(CHPh\,OH)_2$, and he concluded that Legler's compound was similarly constituted Baeyer[†] obtained a similar compound from hydrogen dioxide and chloral; he showed also that hydrogen dioxide, ammonia, and formaldehyde react to produce hexahydroxymethylene-diamine, a compound which Legler had previously prepared from his product referred to above

Since Legler's compound has been comparatively little studied and its composition and constitution have been only indirectly determined, it appeared of interest to make a more detailed examination of the compound obtained by the direct process mentioned above

The molecular weight was determined by the cryoscopic method, using acetic acid and water as solvents

	Solvent	Solute	Depression	Molecular weight
		In Acetic Acid		
I	17 07	0 1159	0 315	83 8
II	17 07	0 3162	0 795	90 8
III	17 ·07	0 5840	1 410	94 ·6
		In Water		
IV	14 98	0 ·5887	0 75	90 1
V	14 60	0 6645	0 925	92 5

Theory for $H_4C_2O_2.H_2O_2 = 94$

In order to ascertain the stability of the compound in water another determination was made; the solution was then allowed to stand in melting ice, and the freezing point again determined after 24 and 48 hours; the results were as follows —

VI. 0 3459 grm of substance in 16 74 grm of water gave, on dissolution, a depression of $0.425°$ (M.W. = 91). After 24 hours the depression was 0·470, and after 48 hours 0·480 This difference is altogether insignificant,

* 'Annalen,' vol 298, p 202 (1897)
† 'Ber.,' vol. 33, p. 2479 (1900)

and it may be concluded that the compound exists practically unchanged at 0°, at any rate during this interval of time. If the temperature is allowed to rise to that of the laboratory, a considerable increase occurs, thus, the same solution, kept at the ordinary temperature for 48 hours more, gave a total depression of 0 645, corresponding to calculated molecular weight of 60. This result may, of course, be due to partial dissociation, or, more probably, to interaction of the constituents giving rise to formic acid

A further experiment was made in order to ascertain whether a change in molecular concentration occurred after the catalytic destruction of the potential hydrogen dioxide by means of platinum black

VII 0 2447 grm substance in 13 97 grm. of water gave a depression of 0 37° (M W = 89)

About ½ grm of platinum black was then added to the solution, and the mixture was allowed to stand for 24 hours   The total depression was then 0 395°   This difference being not much beyond the limits of experimental error, it may be concluded that the total number of molecules in solution is practically unaltered after the hydrogen dioxide has been eliminated   The solution obtained in this way appears to be pure formaldehyde, and the result could be explained by assuming that it exists in the dimeric form

According to Auerbach and Barschall, however,* formaldehyde in aqueous solution, whether prepared from the gas or from the polymerides, is an equilibrium mixture of the trimeric and monomeric forms, or their hydrates, the proportions being dependent on the temperature and concentration , the above result could, of course, be accounted for in this way

It is probable that this method may be found to be of service for the rapid preparation of pure aqueous solutions of formaldehyde , the catalytic decomposition takes place very rapidly if the solution is gently warmed, but a purer product is obtained if the operation is carried out at 0°.

The behaviour of the solid substance on exposure to light has only been partially studied   When kept for a month in the dark, in a tube closed with cotton wool, the substance was unchanged in appearance, but had lost about 1 per cent of its weight   A corresponding experiment was made in bright sunlight, and in this case the substance became partially liquefied after some days, and gave a strongly acid solution   Exposed to bright sunlight in a sealed tube, it behaved similarly , the gas evolved was hydrogen, containing some carbon dioxide, and the solution was strongly acid.   Probably, however, the change is more complex than the mere resolution into formic acid and hydrogen, since the liquid, on acidification, gives a decided fruity odour resembling acetaldehyde.

* 'Chem Centr.,' vol 2, p 1081 (1905).

If the crystals are exposed to light in an open watch-glass, they show no tendency to liquefy, after a few days they become opaque, owing to finely dispersed gas bubbles, and the crystals then begin to decrepitate in a remarkable way, the smaller crystals being projected about in all directions. Even after six weeks' exposure in this manner, the crystals still give aldehyde and peroxide reactions.

Constitution

Several compounds of organic substances with hydrogen dioxide have been prepared and are usually regarded as containing "hydrogen dioxide of crystallisation"[*]

The nature of such a combination is assumed to be analogous to that of water of crystallisation, one would expect therefore that the compounds would show a readiness to dissociate into their constituents.

Since the compound described in the present communication remains undissociated when dissolved in solvents such as water and acetic acid, it would not appear to belong to this class, and its constitution is more appropriately represented by a structural formula such as that suggested by Nef, namely —

$$CH_2 OH$$
$$|$$
$$O$$
$$|$$
$$O$$
$$|$$
$$CH_2 OH$$
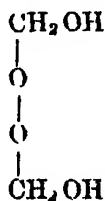
In order to obtain confirmatory evidence of this, an attempt was made to prepare the benzoyl derivative. The compound was dissolved in water, cooled by ice, and treated with benzoyl chloride and sodium hydroxide according to the Baumann-Schotten method. A soft solid product was thus obtained which hardens when dried on filter paper. It was dried over sulphuric acid and solid potash, washed repeatedly with small quantities of anhydrous ether, recrystallised from this solvent, in which it is sparingly soluble, and kept in a vacuum desiccator.

The product crystallises in octahedra and melts at about 103°. When heated a little above this temperature it decomposes with explosion, giving yellow vapours.

Analysis of this product, and its general properties, show that it is *benzoyl peroxide*, so that the experiment is merely confirmatory of the peroxide character of the original substance.

[*] Compare, for example, Tanatar, 'Chem. Centr,' vol. 2, p 583 (1906)

Summary and Conclusions

Formaldehyde and hydrogen dioxide combine together directly when a mixture of their solutions is concentrated *in vacuo*, to form a definite crystalline compound having the molecular formula $2\,H\,CHO\,H_2O_2$. This compound shows unexpected stability, it undergoes little, if any, change when kept in the dark at the ordinary temperature, and it dissolves unchanged in water or acetic acid It gives the normal molecular weight by the cryoscopic method, and this value, in aqueous solution, is not changed after 48 hours at 0°.

The crystals are explosive when heated to about 70° and they take fire in contact with reduced iron or platinum black They undergo slow decomposition when exposed to bright sunlight

Treatment of the aqueous solution with platinum black causes a rapid decomposition of the potential hydrogen dioxide and a pure solution of formaldehyde remains

The general behaviour of the substance leads to the conclusion that it is not one containing hydrogen dioxide of crystallisation, and is rather to be regarded as an "atomic" compound in the ordinary sense of the term

There seems to be no doubt that the compound is identical with that which Legler, in 1881, obtained amongst the products of slow oxidation of ether

Absorption of Gases in the Discharge Tube.

By F. H. Newman, A.R.C.S., B.Sc.

§ 1. Introduction.

Mey[*] has shown that when the liquid alloy of sodium and potassium is made the cathode in a discharge tube, then, on passage of a current, if the gases nitrogen and hydrogen are present they are absorbed. The inactive gases, such as helium, are not affected, however, so he concludes that this would form a very convenient method for the preparation of helium where hydrogen and nitrogen are present as impurities. He mentions the rate of absorption compared with the quantity of electricity passing, and it is much larger than the absorption of gases by the walls of the discharge tube during the passage of a discharge. It is thought that the gases form chemical compounds with the sodium and potassium—the nitrogen giving the nitride and hydrogen the hydride.

The following experiments were made to see if there were any relation between the amount of gas absorbed and the quantity of electricity passing during discharge—the measurements being made with varying pressures of the gas. In order to measure the electricity a small voltameter containing sulphuric acid was employed, and the quantity of hydrogen evolved in it was compared with the amount of gas absorbed. The current employed had to be a uni-directional high-tension one. For this, an induction coil with an Oliver Lodge valve in the secondary was used. Provided the current was not too large this arrangement gave satisfactory results.

§ 2. Preliminary Experiment.

Fig. 1 shows the apparatus used at first. The nitrogen was prepared in a vessel, A, by allowing air to stand over phosphorus for several hours. The gas then passed over phosphorus pentoxide and so into a calibrated reservoir B, from which it entered the discharge tube, being fed in by manipulation of the head of mercury. C was an oil gauge which gave the absolute pressure of the gas. Castor oil was originally used in the manometer, but later Fleuss oil was substituted, as it did not contain much air, and moreover was more sensitive. The alloy, when placed in the apparatus, became coated with the oxide, but it was found that if a discharge was passed in rarefied nitrogen the

scum at the surface of the alloy disappeared with a little shaking, leaving a bright layer   In making a determination with the metal as cathode, the apparatus having been exhausted by means of a Toepler pump, a small quantity of nitrogen passed into the apparatus   By altering the level of the mercury in B the pressure was kept constant during absorption, and from the initial and final readings of the volume of gas in B the amount of nitrogen which had been absorbed at the indicated pressure was noted   This was
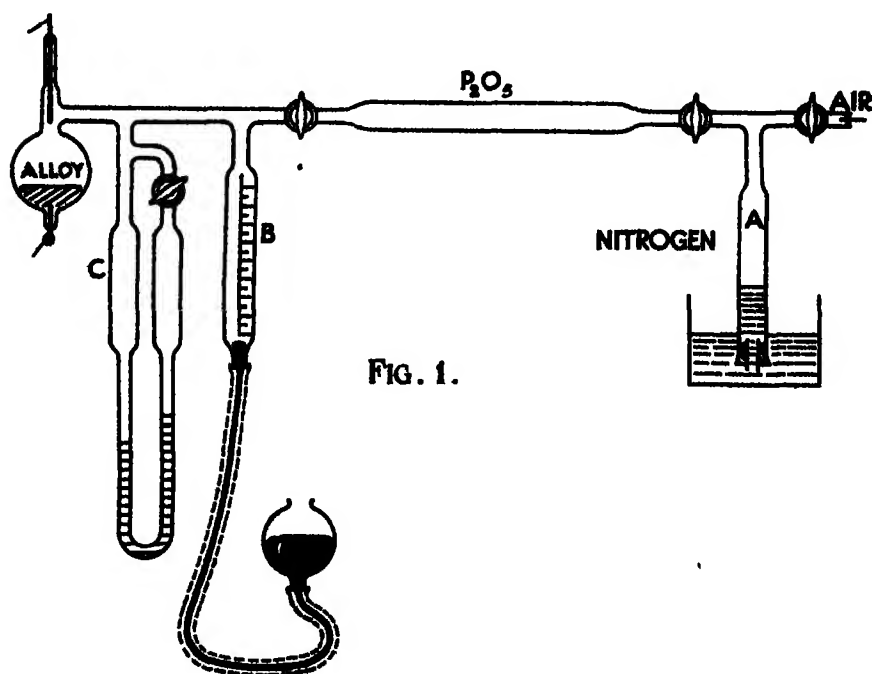
FIG. 1.

then compared with the volume of hydrogen which had been liberated in the voltameter

This method of feeding in the nitrogen gave unsatisfactory results owing to the lack of sensitiveness of the oil in the manometer, for it was found impossible to supply the nitrogen at such a rate that the pressure remained constant throughout.   Hence the amount of gas indicated by B was not the true quantity which had been absorbed.   The following method of feeding in the nitrogen was then substituted

§ 3. *Absorption of Nitrogen and Hydrogen*

In this method the apparatus shown in fig 2 was employed   The reservoir was removed and in its place a known small volume between two taps T_1 and and T_2 was used.   By opening T_1 and then closing it a known volume of gas

practically at atmospheric pressure is enclosed between T_1 and T_2. On opening T_2 the gas will fill the apparatus and the alteration in pressure which it produces can be read from the mano-meter. By allowing several volumes to enter in this way, and noting the pressure before and after, the amount of gas which causes a recorded difference of pressure —read from the gauge—is found. Thus, when absorption takes place, from the initial and final readings of the mano-meter, the amount of gas at atmospheric pressure which has disappeared is obtained immediately. In this way several determinations of the quantity of nitrogen absorbed using the alloy as cathode were made over a wide range of pressures.
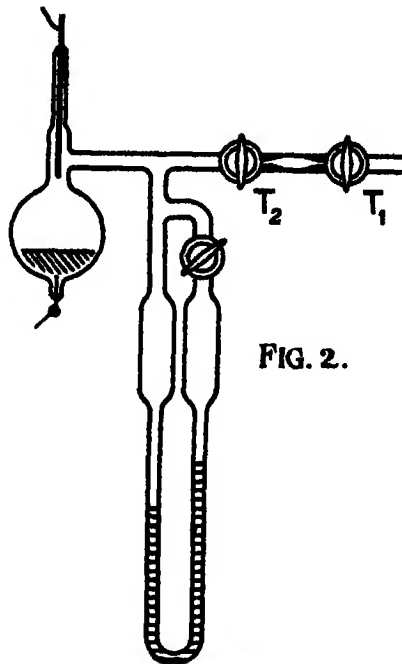
Mey only states there is absorption when the alloy is made the cathode, but it was found that such was the case when it formed the anode, although the amount of gas absorbed relative to the quantity of electricity passing in the circuit was not as great as when used as the cathode. A series of observations were made with the alloy as the anode. It must be mentioned that the surface of the metal remained clear however long the discharge was passing, and there appeared to be no diminution in the rate of absorption of the nitrogen.

These determinations finished, hydrogen was next tested. The gas prepared by the action of sulphuric acid on zinc passed over phosphorus to remove any oxygen, and also over phosphorus pentoxide. With this gas, and the alloy forming first the cathode and then the anode, measurements were taken at various pressures. The surface of the metal did not remain clear as it had done when nitrogen was used, but became coated with a black scum which suggested the presence of the hydrides of sodium and potassium. Thus it was necessary to keep the surface clean by continual shaking. On substi-tuting discharge tubes of different shapes the results were found to be independent of the surface area of the alloy, thereby suggesting that the relation between the amount of gas absorbed and the quantity of electricity is independent of the extent of the surface of the alloy. It was also shown that if aluminium electrodes were used in a bulb-shaped vessel with a pool of

FIG. 2.

alloy at the bottom of the bulb, and not in electrical contact with the electrodes, then absorption of nitrogen and hydrogen resulted when a current was sent through the gas

§ 4   *Absorption of Oxygen by Mercury*

Stark[*] has observed that when mercury is placed near the cathode in a discharge tube absorption of nitrogen and oxygen results, with the probable formation of mercury oxide and nitride   Mercury was substituted for the alloy, and, using oxygen obtained from a cylinder, similar experiments were made to those described above   Absorption resulted whether mercury formed the cathode or the anode   Since the mercury became coated with a scum, the formation of the compound of mercury with oxygen probably takes place at the surface of the metal.   The inside of the tube received a reddish deposit of mercury oxide as observed by Stark, so that the chemical action also takes place throughout the gaseous volume

With nitrogen instead of oxygen very little absorption resulted when the ordinary discharge was employed, but with a condensed discharge the effect was greatly increased

§ 5   *Tabulation of Results.*

A few of the results obtained in the experiments described above are shown in the following tables.   The current in the secondary varied from 0·005 to 0·010 ampère

Table I —Absorption of Nitrogen by the Sodium-Potassium Alloy

Alloy used as cathode				Alloy used as anode			
Volume of N₂ absorbed (A)	Pressure	Volume of H₂ liberated in volta meter (B)	Value, A/B	Volume of N₂ absorbed (A)	Pressure	Volume of H₂ liberated in volta meter (B)	Value, A/B.
c c	mm Hg	c c		c c	mm. Hg	c c	
0·31	14·7	0 16	1·9	0 16	13·4	0·25	0·6
1 37	10 5	0·62	2 2	0 15	12 8	0·17	0 9
0 43	9 9	0 30	2 2	0 16	11·4	0·23	0 7
0 73	5 0	0 31	2 4	0 17	9·9	0 29	0·6
0 39	4·9	0 16	2 4	0 18	7·7	0 27	0·7
0 63	4 1	0 28	2 3	0·20	7 4	0 28	0 7
0 28	4·0	0·09	2·6	0 16	6 2	0 28	0·7
0 30	2·3	0·12	2·5	0·22	6·2	0·31	0 7
0 27	0 8	0 10	2·7	0 21	5 4	0 24	0·9
0 28	0 7	0·10	2·8	0 17	4 4	0·17	1 0
0 18	0·5	0·06	3·0	0 27	2 7	0 15	1·8
0·24	0 3	0·06	3·0	0 15	1 2	0·07	2·1

* 'Phys. Zeit.,' vol. 14, p. 417 (1913).

Table II.—Absorption of Hydrogen by the Sodium-Potassium Alloy.

Alloy used as cathode				Alloy used as anode			
Volume of H₂ absorbed (A)	Pressure	Volume of H₂ liberated in voltameter (B)	Value A/B	Volume of H₂ absorbed (A)	Pressure	Volume of H₂ liberated in voltameter (B)	Value A/B
c c	mm Hg	c c		c c	mm Hg	c c	
0 45	10 ·0	0 31	1 5	0 36	7 2	0 44	0 8
0 64	8 6	0 29	2 2	0 33	6 1	0 48	0 7
0 80	6 8	0 29	2 8	0 ·26	5 ·9	0 47	0 ·6
0 73	4 9	0 25	2 9	0 30	4 8	0 48	0 6
0 54	4 6	0 18	3 ·0	0 37	4 ·0	0 65	0 6
0 40	4 4	0 14	2 9	0 42	2 7	0 50	0 8
0 53	3 9	0 18	2 ·9	0 38	2 4	0 56	0 7
0 74	3 ·0	0 23	3 2	0 38	1 7	0 48	0 8
0 ·72	2 8	0 22	3 3	0 28	1 4	0 29	1 ·0
0 ·60	1 2	0 19	3 2	0 28	1 2	0 22	1 3
0 30	1 ·0	0 09	3 3	0 25	1 0	0 20	1 ·3
0 14	0 4	0 ·04	3 5	0 20	0 8	0 13	1 5

Table III.—Absorption of Oxygen by Mercury

Mercury used as cathode				Mercury used as anode			
Volume of O₂ absorbed (A)	Pressure	Volume of H₂ liberated in voltameter (B)	Value A/B	Volume of O₂ absorbed (A)	Pressure	Volume of H₂ liberated in voltameter (B)	Value A/B
c c	mm. Hg	c c		c c	mm Hg	c c	
0 ·16	10 ·0	0 25	0 6	0 14	10 5	0 ·27	0 5
0 ·15	9 8	0 22	0 7	0 11	8 6	0 22	0 5
0 16	8 ·5	0 27	0 ·6	0 17	7 ·6	0 33	0 ·5
0 16	8 ·3	0 21	0 8	0 14	6 3	0 27	0 5
0 14	7 ·0	0 ·24	0 6	0 12	5 4	0 21	0 ·6
0 18	6 ·0	0 27	0 7	0 14	4 2	0 25	0 ·6
0 17	5 ·0	0 22	0 ·8	0 12	3 ·6	0 14	0 ·9
0 ·18	4 8	0 18	1 ·0	0 ·09	2 ·7	0 10	0 9
0 22	3 2	0 10	2 2	0 13	2 1	0 12	1 1
0 ·24	2 8	0 10	2 4	0 18	0 12	0 10	1 3
0 30	2 2	0 10	3 ·0	0 13	0 11	0 11	1 ·2
0 22	1 6	0 07	3 ·1	0 ·021	0 ·07	0 ·013	1 ·6

§ 6. *Discussion of Results.*

Stark has suggested that the absorption of nitrogen and oxygen in the presence of mercury in the discharge tube is due probably to the action of dissociated molecules of these gases, *i.c.* atomic gases, and when in this state

the gas is more active than under ordinary conditions Prof R. J Strutt[*] has shown that there is a chemically active modification of nitrogen, so that all the results obtained above can be explained by assuming that, under the influence of the electric discharge, active gas is produced   That the nitrides of sodium and potassium are formed by the absorption of nitrogen can be shown by passing moist air over the alloy into water and applying the Nessler test for ammonia to the latter This suggested that, if the production of these nitrides were due to active gas, then passage of the afterglow obtained in the case of active nitrogen over the sodium-potassium alloy should produce nitrides of these metals

The apparatus used is shown in fig 3   Nitrogen obtained from a cylinder stood over phosphorus for several hours to remove all oxygen, and the flow was regulated by means of taps, so that 3 or 4 litres per hour passed through

FIG. 3.
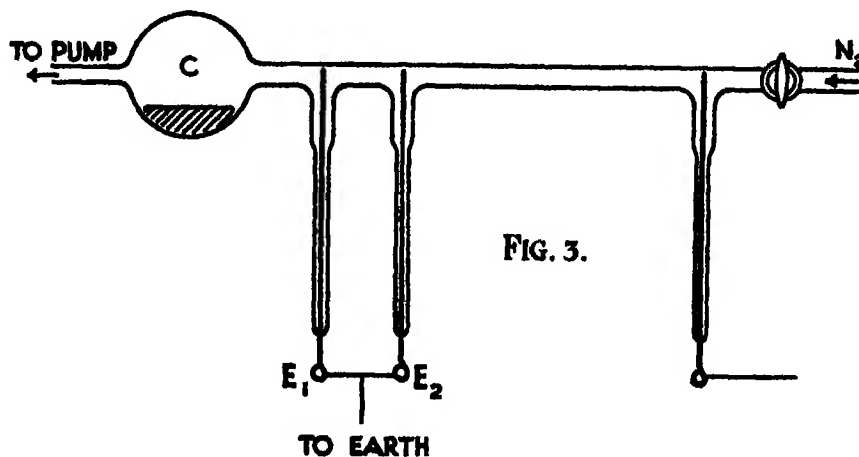
the apparatus, being drawn off by a pump   The two electrodes, E_1, E_2, were connected together and put to earth, in order to eliminate stray discharge— one end of the secondary circuit also being earthed   The alloy was placed in a bulb, which was sealed to the vessel C Being exposed to the air, it became coated with the oxide, but, on evacuation of the apparatus, by turning the latter so that the alloy flowed into C under a vacuum a clear surface was obtained   A condensed discharge was used, and active nitrogen allowed to flow over the metal for half an hour, the alloy being vigorously shaken in the meantime   A blank experiment was then made by passing the nitrogen over some alloy without the discharge.   The two portions were then tested for the presence of nitrides by passing moist air over the surface, and making the Nessler test for ammonia.   A copious precipitate was

* Bakerian Lecture, 'Roy. Soc. Proc.,' A, vol. 85, p. 219 (1911).

obtained in the case of the alloy which had been subjected to the action of the active nitrogen, whereas no such precipitate was found where the ordinary nitrogen was used. This proves that the active modification of nitrogen is absorbed by the alloy, and so gives strength to the theory that the general case of absorption is due to active modifications of gases produced by the electric discharge. It must be mentioned that no stray discharge passed into the alloy bulb C.

If the gases assume an active modification, the results above are easily explained. As the pressure decreases, the velocity of the electrons becomes greater, and, as it is these which by their collisions with the molecules of the gas produce the active modification, a larger quantity of the latter, compared with the quantity of electricity employed, would be produced at these lower pressures.

It will be observed that greater absorption always takes place at the cathode. Two reasons might be put forward in explanation. Owing to the large electric force in the neighbourhood of the cathode, with the resulting high velocity of the electrons, it is probable that most of the active gas is produced at this part of the discharge tube, so there would be more near the alloy when it forms the cathode than when it is the anode.

The absorption of the positive rays would provide another explanation. When these rays were allowed to fall on a pool of alloy placed at the bottom of the discharge tube, absorption of nitrogen resulted. However, the question as to whether the rays themselves are absorbed, or the active gas produced by them, is still undecided. In all probability it is the former, for the amount of active nitrogen produced by the collisions of the positive rays with the molecules of the gas would appear to be small.

§ 7   *Other Experiments*

Other metals in the molten condition, including cadmium, zinc, bismuth, and lead, were tested for absorption of nitrogen, but no positive result was obtained with the ordinary discharge. This might be explained by the decomposition of any nitrides produced owing to the high temperatures, or the active gas might not be able to reach the molten metal owing to the presence of vapour of the metal above the surface.

§ 8. *Summary.*

1. The sodium-potassium alloy not only absorbs nitrogen and hydrogen when used as the cathode, but also when it forms the anode in a discharge tube, although the absorption relative to the quantity of electricity passing is greater in the first case than in the second.

2 Mercury absorbs oxygen in a similar manner.

3 In all cases the absorption relative to the electricity increases as the pressure decreases.

4 The gases probably assume active modifications under the influence of the electric discharge   This supposition is strengthened by the observation that the known active modification of nitrogen is absorbed when passed over the alloy

5 The greater absorption, when the metals are used as the cathode, is due probably to the combination of the positive rays with the metal.

In conclusion, I wish to express my gratitude to Prof R J Strutt, F R S , at whose suggestion the above investigation was undertaken, for his kind help and interest throughout the course of the research

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Photographic Analysis of Explosions in the Magnetic Field.

By Prof. Harold B Dixon, F R S , C Campbell, M Sc , and W E. Slater, B Sc

(Received June 11,—Read June 18, 1914)

[Plates 5–8]

Introductory

In a discussion on Gaseous Combustion with particular reference to explosions, at the British Association Meeting at Sheffield, 1910, Sir J. J Thomson called attention to the fact that combustion is concerned not only with atoms and molecules, but also with electrons moving with very high velocities   In the "surface combustions" studied by Prof. Bone it appeared probable that the streams of electrons known to be emitted by incandescent surfaces promoted combustion by electrifying the contiguous layers of gas, and the great rapidity of combustion in the explosion-wave might be due to the molecules at the moment of combustion sending out electrons with very high velocities.   These may precede the explosion-wave and prepare the way for it by ionising the gas.   But the motion of the ions can be stopped at once by means of a transverse magnetic field, in which they curl up and are caused to revolve in small circles.   He therefore thought it would be of very great interest if Prof. Dixon would repeat his experiments on the photo-

graphy of the explosion-wave under such conditions as to determine whether the form of the wave could be modified by a magnetic field

He further suggested that the phenomena of the damping of the velocity of electrons and the initiation of chemical change by small quantities of moisture might be closely related

Sir J J Thomson's suggestion, the importance of which was emphasised by other physicists, led us to make several attempts to detect the effect of a magnetic field on the propagation of an explosion-wave   No effect could be detected with a short but intense field, or with a more extended but less intense field   But we were unwilling to publish negative results until we had experimented with a more powerful magnet   Then by the kindness of Sir Ernest Rutherford we were allowed the use of one of the two new magnets he constructed last year for the very purpose we had in view—that of deflecting electrons of high velocity

This magnet had a longer and more intense held than either of the two we had previously used

Description of Magnets.

Three series of experiments 'with three different electromagnets were carried out

In the first series the magnet used was of a moderate size, being capable of taking a voltage of 100 and a current of 15 ampères   The field was concentrated by using very narrow pole-pieces, so that, although very intense, it
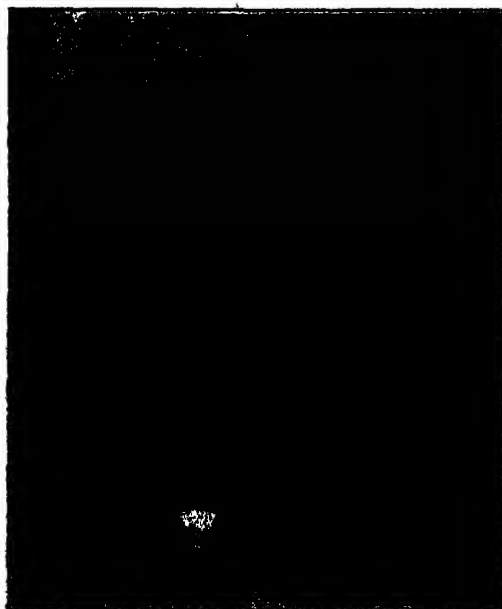
only covered about 3 cm of the explosion tube. With a gap of 2 cm. between the poles, the intensity of the field obtained was about 8000 gauss.

The magnet used in the second series was similar in size, but with much larger pole-pieces, the field being spread out over about 40 sq cm The field obtained was therefore much less intense but more extended than with the first magnet With a voltage of 60, a current of 10 amperes and a gap of 2 cm. between the poles, a field of 1500 gauss was obtained.

The magnet used in the third series was much more powerful than either of the above The core was of the softest iron procurable, and of very high permeability. Each arm of the core carried a bobbin of brass with 1500 turns of thick copper wire, making a total for the entire magnet of over 3000 turns

The pole-pieces, which were fixed in position by means of the large iron bolts as shown, were cut from rectangular blocks of soft iron of measurements 10 cm wide, 16 5 cm deep and 17 cm. long Each pole-piece was bevelled along one side, so that the field was concentrated between two surfaces of 5 cm × 17 cm The gap used was about 2 cm Under these conditions, and with an E.M F of 100 volts and a current of 7 amperes the intensity of the field was found by means of a fluxmeter to be 10,000 gauss Through 17 cm of this field the explosion was made to travel.

To obtain a practical test of the efficiency of the magnet in deflecting a stream of electrons, its effect on the β-rays from radium was tried A tube of radium bromide was placed at one end of the field and a barium platino-cyanide screen at the other Before' turning on the current, the phosphorescence produced by the rays was easily visible, but immediately the magnet was made, it disappeared. The experiment was repeated with the screen at a distance of 10 mm. from the radium. Again every ray was taken out Finally, by bending the screen into a half-tube and by placing the radium in the axis of it, it was found that all the rays were so deflected that no point on screen more than 2 mm. in front of the radium was affected

Arrangement of the Magnets.

The magnets were arranged similarly to the one shown in the photograph, one pole-piece standing directly above the other in such a way as to allow the explosion tube to pass horizontally between the two. In each case the distance between the pole-pieces was 2 cm., being just sufficient to admit the glass tube

With the two smaller magnets, thin wooden props were placed at each corner of the poles to act as reference marks.

In the case of the third magnet, small brass pillars were substituted for the

wooden props, to serve the purpose of supports, the iron bolts being insufficient to withstand the mutual attraction of the poles.   These pillars appear in the photographs as two dark vertical bands, the thinner one being the nearer to the starting point of the detonation wave

The height of the magnets was adjusted so that the part of the tube running between the poles was at right angles with the camera, and in the same horizontal plane

The distance between the tube and the camera was such that about 10 cm of the tube on each side of the poles should appear on the photograph

Arrangement of Tubes, etc

The tube in which the explosion was made to travel consisted of a lead pipe, of length 130 cm and internal bore 1 2 cm   At one end of this was a brass ferrule into which was fixed by means of Faraday cement a strong glass tube of length 68 cm and internal bore 1 2 cm   At the other end was the sparking arrangement (a glass firing-piece carrying two platinum terminals) and a brass tap through which the tube was filled   By this means time was allowed for the explosion to set up the detonation wave before reaching the magnetic field.

In the experiments on the initiation of the flame, the platinum terminals were fused into the glass tube in which the explosion was photographed, the spark being passed in some cases between the poles of the magnet, in others about 1 inch beyond them

In all cases the mixture was fired by a discharge from a Ruhmkorff coil, which was started by means of a switch near the camera.

The Photographic Apparatus

The camera was similar to the one used in previous experiments on the photographic analysis of explosions

It consisted essentially of a stout light-proof box fitted with an adjustable lens which could be focussed on to a rapidly revolving wheel carrying the film.   This wheel was 1 metre in circumference and could be rotated by means of suitable gearing at a speed of about 80 revolutions per second.

Eastman's N C films were found to be the most suitable for the purpose

Description of an Experiment.

The method of carrying out an experiment was as follows :—

The camera having been focussed on the portion of the tube passing between the magnetic poles, the tube was swept out and filled with the previously prepared mixture, and a cork inserted in the free end of the glass tube.

In experiments with the less violent mixtures such as $2CO + O_2$ and $H_2 + 2O_2$, the cork was firmly fixed but with the more violent mixtures it was inserted loosely and allowed to be blown out.

The room was then darkened and the film fixed on the wheel and rotated The speed of the wheel was not determined accurately, but a rough measurement showed that in all these experiments the wheel performed about 40 revolutions per second, corresponding with a velocity for the film of 40 metres per second As soon as the wheel was rotating uniformly, the current was switched on to the magnet and the mixture fired.

The experiment was then repeated under exactly the same conditions, except that no current was sent through the magnet By this means pictures were obtained of explosions of the same mixture with and without the magnet, other conditions being the same These could then be compared and any difference between them noted The films were developed and fixed in the usual manner

Description of the Photographs (Plates 5-8)

The photographs reproduced show the movements of the flames of different gaseous mixtures analysed by the rotation of the film

(1) The explosion-waves in the following mixtures were photographed as they entered, traversed and emerged from the magnetic field, and again when they travelled through the same tube without the magnet being made —

α. Cyanogen and oxygen with different proportions of nitrogen

β. Hydrogen and oxygen in different proportions

γ Acetylene and oxygen

δ Carbon disulphide and oxygen

ϵ Carbon monoxide and oxygen.

In Photographs 1 and 2 the explosion-waves in equal volumes of cyanogen, oxygen, and nitrogen are shown The wave travelling from right to left at a uniform velocity makes a straight inclined line at the bottom of the picture, the inclination depending on the horizontal velocity of the image of the explosion-wave and on the vertical velocity of the film The entrance to the magnetic field is marked by the first vertical dark line on the photograph made by the small brass pillar (which helps to separate the magnets) obscuring the light in the tube behind it The flame is seen to continue in the same straight line and with the same brightness as before, and therefore with the same velocity and intensity through the magnetic field, and after passing the second vertical dark line, made by the corresponding brass pillar at the further end of the magnet, to continue its course without alteration. The inclined line stretching from left to right above the first is

caused by the reflection from the cork at the end of the tube This reflected wave (travelling, of course, more slowly than the explosion wave) appears also to be unaffected by the magnetic field The companion photograph shows the progress of the explosion wave and the return of the reflected wave in the same mixture without the magnet being made. No difference due to the magnetic field can be detected

Photographs 3 and 4 show the explosion-waves in electrolytic gas The flames travel, as before, from right to left, and the reflected waves return, later, from left to right No difference due to the magnetic field can be detected

Photographs 5 and 6, acetylene and oxygen, and 7 and 8, carbon disulphide and oxygen, show more detail, as the flames are brighter and more prolonged In each case a second reflected wave, travelling in the same direction as the original explosion wave (from right to left), is visible high up in the photographs The magnetic field has no visible influence

Photographs 9 and 10 show the explosion-waves in carbon monoxide and oxygen In this mixture—where water vapour is necessary for the propagation of the explosion and a wider scope for the action of electrons might be presumed—there is still nothing which can be attributed to the magnetic field Comparative experiments with the moist and dried gases—the dried mixture having stood over oil of vitriol—showed no difference as the flames traversed the magnetic field (Photographs 11 and 12)

(2) Lastly, the effect of the magnetic field on the initiatory phases of explosion flames was studied. The photographs reproduced show (13 and 14) the flame in acetylene and oxygen initiated by a spark just outside (to the left) of the magnetic field The flame as it spreads to the right enters and passes through the field, its acceleration being unaffected by the magnet The explosion-wave is not set up before the flame has passed beyond the range of the photograph.

Photographs 15 and 16 show the same mixture (acetylene and oxygen) fired by a spark in the centre of the picture between the magnetic poles The flames spread in the same way whether the magnet is on or off The central (faint) perpendicular band is due to distortion of the glass tube where the platinum wire is fused in.

Since the powerful magnetic field employed produced no visible effect with any gas mixture, and since the mechanism of a compression-wave (liberating the chemical energy as it goes along) accounts in a reasonable way for the phenomena of gas explosions, we see no evidence that convinces us that the velocity of the explosion-wave is due to the ionising action of electrons.

On the Spectrum of Elementary Silicon.

By Sir William Crookes, O M , P R S

Few elements have had so much attention directed to their spectra as silicon, and scarcely any element has shown such diverse results between recorded observations of different observers

Hitherto no observer has recorded a complete table of lines from the shortest ultra-violet to the last pair of lines visible in the red   The values I now give are the result of observations extending over 11 years, during which time the advent of the colour-sensitive plate has made possible photographic records of lines that are visible.

The accurate tabulation of the wave-lengths of lines in the silicon spectrum is of considerable importance in physical astronomy , several stars, especially those of the Orion type, have lines corresponding to lines of silicon   Some years ago whilst studying the lines in a particular part of the silicon spectrum I was surprised to find that lines given by my own spectroscope did not altogether tally with lines in the same part of the spectrum recorded by other observers, some being altogether absent, while the wavelengths of others did not correspond within allowable errors of observation The cause of some of these discrepancies was traced to impurities in the samples of silicon used by myself and others   I endeavoured to clear up these doubtful points by trying to secure elementary silicon in as high a state of purity as possible   Every sample that could be obtained by purchase was tested and found to be far from pure, although impurities were different in kind as well as quantity

Many different samples of fused silicon have been used by me in this research   Most samples were obtained by purchase from dealers in chemicals, rare metals, and their alloys   I could not find a sample sufficiently free from metallic impurity to show no extraneous lines in the spectrum. Some samples gave an excess of one set of lines, while others would give a number of lines due to another impurity. It was evident that all commercial silicons were impure, and the impurities in some samples were different from those in others   At first I started getting the lines actually due to silicon by enlarging the photographed spectra and then comparing the lines they had in common. In this way I got at last a tolerably good map of the silicon lines, which map, however, differed seriously from many maps given by other observers.

The Carborundum Company at Niagara Falls have been making large pans, cylinders, and vessels of fused and cast silicon for the use of manu-

facturing chemists. I wrote to the Niagara firm explaining my difficulties, and asking for silicon of a high degree of purity They courteously replied that it was not possible to manufacture silicon in commercial quantities of a higher degree of purity than 98 per cent, but occasionally they got small specimens occluded in slags assaying 99 per cent and over They sent me three samples having this origin, giving on analysis 99·56, 99 86, and 99 98 per cent of silicon, the impurities being titanium, iron, and aluminium. These samples have been used in correcting the lines given by other less pure samples, and in clearing up doubtful points where impurity would interfere with certainty of identification

Fused silicon is an interesting material, and when pure takes a high polish Used as electrodes with the high frequency current much trouble is caused owing to a coating of oxide that forms almost at once, the spark becoming much less luminous. Under these conditions the surface of the electrodes presents a curious pitted appearance, as shown in fig. 1.
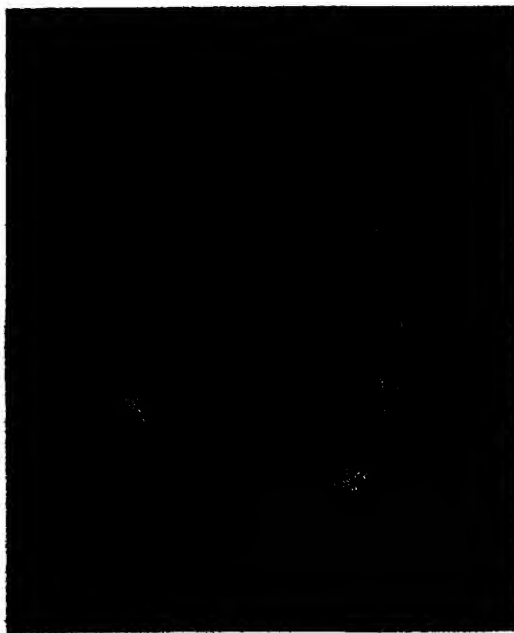
Fig. 1.

After trying many methods for keeping the spark bright, success was achieved by frequently removing the poles and grinding the surfaces with an emery wheel; in some cases where an exposure of seven hours was given a second pair of electrodes was employed, changing every 15 minutes, and re-grinding one pair while the others were sparking.

The instrument used for measuring the lines is that described in my paper " On the Ultra-violet Spectrum of Radium "[*]   In most cases pure iron was used to obtain the standard lines for comparison   Self-induction was introduced by an adjustable coil interposed in the path of the secondary current so as to suppress most of the air lines   The standard lines of iron or other metal selected for comparison with the silicon lines were photographed simultaneously on the same film, so that measurements could be taken in the comparator.   From data so obtained the wave-length of each line was calculated by my son—Bernard H Crookes, M Sc —according to the method given in my paper " On the Ultra-violet Spectrum of Radium "[†]

Recently an improvement has been made in my spectrograph, due to difficulties met with in photographing some of the very faint lines in the silicon spectrum   Long exposures were often necessary, in some cases many hours, and it was found that the variation in the temperature of the laboratory caused sufficient shift in the spectrum to make an otherwise sharp line appear blurred   With my original plan of projecting the two spectra upon the plate in succession by means of stops placed before the slit the temperature variation introduced inaccuracy ; because the standard spectrum of iron or other metal only needed comparatively short exposure, and the room temperature during that period might be different to the mean temperature during the long silicon exposure.

To remove this uncertainty a right-angled quartz reflecting prism is mounted so as to cover the lower half of the slit   The upper half of the slit receives the direct light from the sparking silicon, whilst the light from the standard metal spark is at the side, and is passed into the lower half of the slit by reflection through the right-angled prism.   In this way both the standard and the silicon spark can be photographed simultaneously.   The difficulty introduced by the varying brightness of the two sparks is avoided by adjustable diaphragms mounted between each spark and the slit ; by adjusting these, the light from the brighter spark is reduced so as to equal the fainter one and make the resulting spectra of the same intensity.

The same end may be gained by giving one-half of the exposure necessary for the brighter spark at the commencement, and one-half at the finish   For example, in the case of a seven hours' exposure of silicon, with a vanadium standard that needs only one hour, the exposure is made by starting both sparks simultaneously, and after thirty minutes stopping the vanadium and starting it again after six hours and allowing both to finish together.

[*] 'Roy Soc Proc,' vol. 72, p 295.
[†] *Loc. cit*, p. 302.

In this way any shift of the spectrum due to change of temperature results in an apparent broadening of the lines, and both the standard and the silicon are affected in the same way. The result on the photographic films is shown by two lines of spectra, running parallel to one another and almost, if not quite, touching. In the case of silicon, lines are met in the whole length of the spectrum from high in the ultra-violet through the visible part to the red rays, and it happens occasionally that lines are present where an almost blank space occurs in the iron spectrum; in these cases some other element has to be selected containing spectrum lines in the desired gap. Some of the standard lines chosen have not been measured as accurately as those of iron; therefore my measurements based on such lines have not the same degree of accuracy as the lines measured against an iron standard. In some cases, however, I have been able to re-standardise the lines in the silicon used, by measuring them against iron lines near enough for this purpose, but not near enough to the silicon lines.

There are two lines of silicon in the orange-red portion of the spectrum, extremely faint and hazy in appearance; to get their image with the most sensitive panchromatic films required an exposure of many hours with the 5-prism quartz train. I therefore used for these lines an instrument designed some years ago whereby eye observations could be taken and recorded with the 5-prism spectrograph.

The apparatus shown in outline drawing, fig. 2, takes the place usually occupied by the camera in the 5-prism spectrograph. It consists essentially of a telescope, AB, furnished with the usual micrometer eyepiece, A, and fine wires. The object lens, B, is mounted on an accurately cut screw, C, of one hundredth of an inch pitch, by rotating the screw the lens B is moved sideways so as to traverse the spectrum over the wires in the eyepiece A, the prolongation of the screw C carries a brass drum, D, one inch in diameter, which has ten needle points equally spaced round it. A narrow roll of paper, E, is mounted on a spool just above the drum D, and one end of the paper is pressed on its surface by a soft rubber roller, F. Rotating the drum D therefore draws the paper off the spool E, and imprints on it ten perforations for each revolution of the drum. As one revolution of drum carries the object glass one hundredth of an inch sideways across the lines under measurement, and the drum is one inch in diameter, the space between each perforation equals 1/1000th of an inch movement of the object glass. (The actual distance apart of the dots on the paper is 0 3146 of an inch.) For convenience of calculation one of the needle points is doubled, so as to note each complete revolution. This device of marking the distances on the paper at the same moment as recording the lines eliminates any uncertainty

that would otherwise be due to subsequent unequal alteration in the length of the paper.

The paper band, on its way from the spool E to the drum D, passes over
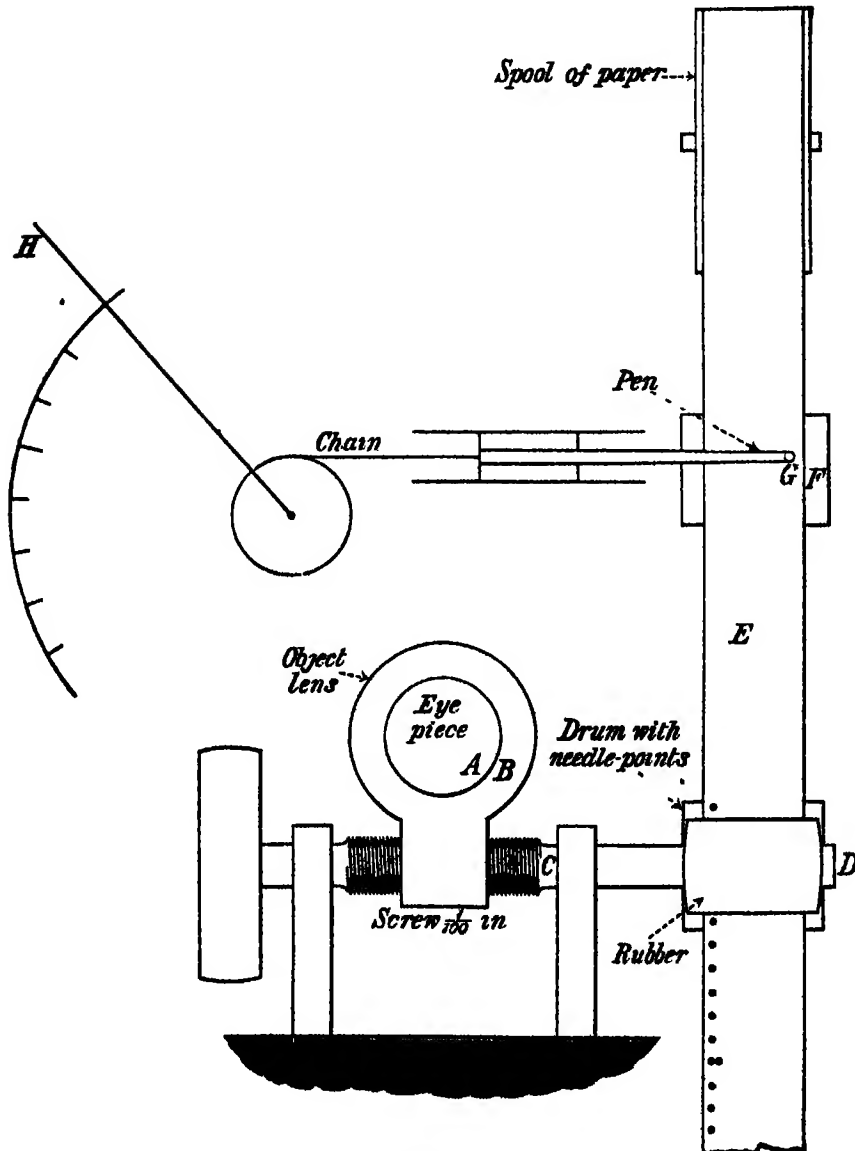
FIG 2

a small table, F, at this point a fine pen, G, carried on a slide, can be made to trace a line any desired length across the strip of paper by pressure of the finger upon the lever H

The method of measurement is as follows —By rotating the screw, the spectrum is made to traverse the field of view, and when the line to be recorded coincides with the fine wires in the eyepiece, a touch of the finger on the lever, H, draws an ink record across the paper strip   When all the lines are recorded the paper strip is removed, and the distance between the dots on the paper can be subdivided into 10 parts by means of a transparent scale, by which the distance apart of any of the recorded lines can easily be measured   From these measurements the wave-lengths of the lines can be calculated in the same way as if the measurements were taken from a photograph   The distance apart of the sodium lines D_1 and D_2, recorded on the paper strip, is 23 mm

A good method of correcting these paper records is to take several observations upon each line in succession, moving the line backwards over the fine wire between each record   In the case of very sharp lines the records practically are in the same place   In other cases the ink lines may not be exactly superposed, because the lines to be measured are faint and hazy, and differences in position of the records are due to the almost insuperable difficulty of the eye hitting on the exact centre of the nebulosity   In such cases accuracy is obtained by taking the mean of the adjacent records of the same line

The first published record of the silicon spectrum is by G Salet in 1873,[*] who gave the wave-lengths of nine lines in the visible part of the spectrum from the orange to violet   His numbers differ from those of later observers, and as there are more accurate determinations of wave-lengths, I have omitted them as of no present value

In 1893 and 1898[†] Rowland published the wave-length of 30 lines occurring in the solar spectrum, ascribed by him to silicon

In 1900[‡] Sir Norman Lockyer gave the wave-lengths of 14 lines in the blue part of the spectrum   He used silicon bromide in a vacuum tube and elementary silicon

In 1901[§] Sir Walter Noel Hartley gave the wave-lengths of eight lines photographically recorded in the ultra-violet part of the spectrum   He obtained them by saturating one of the carbon poles with sodium silicate.

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[*] 'Ann. de Chim et de Phys,' vol 27, p 65
[†] 'A Preliminary Table of Solar Spectrum Wave-lengths,' Chicago , " A New Table of Standard Wave-lengths," 'Phil Trans,' vol. 36, p. 49
[‡] 'Roy. Soc. Proc,' vol 67, p. 403
[§] 'Roy. Soc Proc,' vol. 58, p 179   This paper is a revision, as far as the wave-lengths are concerned, of measurements of the lines published by the same observer in 1883

In 1902* Exner and Haschek published a list of 45 wave-lengths of lines in the silicon spectrum from the extreme ultra-violet to the blue

In 1903† A de Gramont, using elementary silicon and sodium silicate on platinum wire, gave a list of silicon lines partly selected for astronomical comparisons.

In 1905‡ J Lunt gave a list of nine lines of silicon, in the blue portion of the spectrum   These were seen in various vacuum tubes.

In the same year E B Frost and J A. Brown,§ using elementary silicon and titanium prepared in the electric furnace, made careful measurements of three silicon lines selected as being of especial utility in determinations of the radial velocity of numerous stars

In 1908|| de Gramont, in conjunction with C de Watteville, using silicon poles in an atmosphere of hydrogen, published a further list of 23 lines ranging from the extreme ultra-violet to the point in the violet where de Gramont's earlier list commenced

In 1911¶ Eder and Valenta published a list of 28 lines in the silicon spectrum, mostly in the ultra-violet portion and extending down to the blue

In the Tables which follow I give the wave-lengths of the silicon lines measured by the observers named above   Earlier spectrum observations were necessarily imperfect, chiefly because of the difficulty in getting elementary silicon even in an approximate state of purity   Some observers also have limited the range of their observations to a small part of the spectrum, for astronomical and other reasons

* 'Wellenlangen Tabellen für Spektral-analytische Untersuchungen,' Leipzig and Wien

† 'Chemical News,' vol 88, p 238   A paper read before the British Association, Southport Meeting

‡ 'Roy Soc Proc.,' vol 76, p. 118

§ 'Astrophysical Journal,' vol. 22, pp 157, 260

|| 'Comptes Rendus,' vol 147, p 239.

¶ 'Atlas Typischer Spectren,' Wien.

Wave-lengths of the Lines in the Visible Part of the Spectrum of Silicon

Rowland. 1893.	Lockyer 1900.	Exner and Haschek. 1902	De Gramont. 1903	Lunt. 1905	Frost and Brown. 1905	Eder and Valenta. 1911	Crookes 1914 Pure elementary silicon	Remarks
—	3853·9	3853·62	—	—	—	3854·00	3853·812	This is a well defined group of one sharp line followed by two broad nebulous bands The first of these bands at 3856 193 is the strongest. I find no evidence on any of my photographs of the line given by Exner and Haschek at 3853·62 My line at 3853 812 is certainly not a double one
—	—	3854·02	—	—	—	—	—	
—	3856·1	3856·19	3856·0	—	—	3856·20	3856·193	
—	3863·7	3862·80	3862·5	—	—	3862·75	3862·743	
—	—	3883·46	—	—	—	—	—	The line given by Exner and Haschek at 3883 46 is not shown on my photographs, and Lunt ('Roy Soc Proc', vol 76, p 122) regards it as an impurity
3905·680	3905·8	3905·71	3905·5	—	—	3905·80	3905·726	
—	—	4021·0	—	—	—	—	—	
—	4080·0	4030·1	—	—	—	—	—	
—	4089·1	—	—	4089·0	—	—	4089·016	I can find no evidence of either of these three lines on my photographs
—	4096·9	4096·8	—	—	—	—	4097·021	
4103·097	4103·2	4103·2	—	—	—	—	—	
—	—	4103·7	—	—	—	—	—	
—	4116·4	—	—	4116·0	—	—	—	
—	4128·1	4128·1	4128·0	4128·0	—	4128·2	4128·189	Lunt gives these as a pair of "new silicon lines" ('Roy Soc Proc', vol 77, p 125) I find no trace of them on my photographs
—	4131·1	4131·0	4131·0	4131·0	—	4131·0	4131·192	
—	—	—	—	4191·0	—	—	—	
—	—	—	—	4198·0	—	—	—	
—	4552·8	4552·75	4552·5	4553·0	4552·64	—	4552·811	
—	4568·0	4567·95	4567·0	4568·0	4567·90	—	4568·123	
—	4574·9	4574·9	4574·5	4575·0	4574·79	—	4574·823	I cannot see a trace of a line near 4764 20 on my photographs
—	—	4764·20	—	—	—	—	—	
5045·630	5042	—	5045·5	—	—	—	5042·715	This group of seven lines is ascribed by Rowland to silicon, but I find no trace of them on my photographs
5065·775	5057	—	5059·8	—	—	—	5057·832	
5684·710	—	—	—	—	—	—	—	
5690·646	—	—	—	—	—	—	—	
5701·328	—	—	—	—	—	—	—	
5708·632	—	—	—	—	—	—	—	
5772·364	—	—	—	—	—	—	—	
5948·765	—	—	5960	—	—	—	5961·6	These two lines are faint and very nebulous They were measured by means of the recording instrument described in this paper
—	—	—	5879	—	—	—	5962·0	
6343·2*	—	—	6342	—	—	—	6346·962	These are a pair of strong lines in the red They were measured from photographs taken on panchromatic films, giving seven hours' exposure
6869·7*	—	—	6370	—	—	—	6371·032	

* These two lines are ascribed to Rowland by Dr Marshall Watts, Appendix U, p 4.

Silicon Spectrum Lines in the Ultra-violet Portion

Rowland 1893	Hartley 1901	Exner and Haschek 1902	De Gramont 1903	De Gramont and C de Waterville 1908	Eder and Valenta 1911	Crookes 1914, Pure elementary silicon	Remarks
—	—	—	—	—	1929·0	—	This is beyond range of my spectrograph
—	—	—	—	2123·0	2123·8	2124·163	
2208·030	—	2208·1	—	2208·8	2208·1	2208·048	
2210·939	—	2210·97	—	2211·0	2210·0	2210·987	
2211·759	—	2211·84	—	2212·0	2211·8	2211·839	
2216·760	—	2216·76	—	2217·2	2216·76	2216·882	
2218·140	—	—	—	2218·7	—	2218·227	
—	—	—	—	2219·5	—	—	These two lines do not appear on my photographs No observers but De Gramont and C de Waterville have recorded them
—	—	—	—	2303·8	—	—	
2435·247	—	2435·22	—	2435·6	2435·25	2435·212	
2438·864	—	2438·87	—	2439·4	2438·86	2438·911	
2443·460	—	2443·47	—	2443·5	2443·46	2443·464	
—	—	2445·63	—	—	—	—	
2452·219	—	2452·28	—	2452·5	2452·22	2452·219	These two lines do not appear on my photographs They are only recorded by Exner and Haschek, and are recorded as of intensity (1)
2506·994	2506·8	2507·01	—	2506·8	2506·99	2507·055	
2514·417	2514·0	2514·41	—	2514·3	2514·43	2514·406	
2516·210	2515·9	2516·26	—	2516·0	2516·21	2516·131	
2519·297	2518·9	2519·30	—	2519·2	2519·30	2519·276	
2524·206	2523·9	2524·21	—	2524·3	2524·21	2524·110	
2528·599	2528·6	2528·60	—	2529·0	2528·60	2528·585	
—	—	2532·45	—	2533·0	—	*	
—	—	—	—	2535·0	—	—	
—	—	2541·90	—	—	2541·89	2541·970	No trace of a line is shown on my photographs near this spot.
—	—	2608·85	—	2569·0	—	*	
2631·392	2631·8	2631·88	—	—	2631·39	2631·570	
2881·695	2881·5	2881·73	—	2881·7	2881·70	2881·690	
2987·766	—	2987·77	—	2987·8	2987·77	2987·750	
—	—	3086·8	3067·2	—	—	3086·479	
—	—	3093·8	3094·5	—	—	3093·694	
—	—	—	—	—	—	3247·694	
—	—	—	—	—	—	3488·444	
—	—	3591·0	—	*	—	*	
—	—	3791·8	3791·5	—	3791·1	—	
—	—	3796·50	3796·0	—	3795·9	3796·364	There is no trace of a line here on my photographs
—	—	—	3807·0	—	—	—	
—	—	3906·90	—	—	—	3906·802	
—	—	—	3935·0	—	—	—	

* On examining my photographs under high magnifying power very faint lines can be seen in about these positions, but they are too faint to admit of trustworthy measurement.

The Excitation of γ-Rays by β-Rays

By H Richardson, M Sc., Beyer Fellow, University of Manchester

The excitation of γ-rays by the impact of β-rays on different substances has been investigated by several observers   The question was first systematically examined by J A Gray   He showed that penetrating γ-rays are produced by the β-rays of radium E when they impinge on different materials, the amount of γ-radiation increasing with increase of atomic weight of the material * The particular disposition used in his first experiments was not suitable for the examination of any soft types of radiation which might have been excited, but in later work he showed, for the first time, that characteristic radiations were excited in the case of silver, tin, barium and cerium † Chadwick,‡ using the balance method of Rutherford and Chadwick,§ examined whether the β-rays from radium B and radium C excite penetrating γ-rays in different kinds of matter Definite evidence was obtained that an excited radiation amounting to about 0 5 per cent of the primary γ-radiation is produced.   This method, however, was not suitable for the detection of soft characteristic radiations   These general results have recently been confirmed by Starke,|| using the β-rays from a strong preparation of mesothorium

In previous papers by Rutherford and the author on the analysis of the γ-rays from radioactive substances,¶ it has been shown that the γ-rays emitted by the different products can be separated into groups differing widely in penetrating power. Some of these radiations appear to be characteristic of the elements by which they are emitted and fall into one or other of the series given by Barkla.** On the other hand, some of the groups of rays found do not appear to belong to either series.   It was further shown in previous work that when radium C is deposited on nickel a soft radiation is given out which is entirely absorbed by 2 mm.

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* J A Gray, 'Roy Soc. Proc,' A, vol 85, p 131
† J. A Gray, 'Roy. Soc. Proc.,' A, vol. 87, p. 489
‡ J Chadwick, 'Phil. Mag,' vol 24, p. 594 (1912).
§ Rutherford and Chadwick, 'Phys. Soc. Proc,' April, 1912
|| Starke, 'Phys Zeit.,' vol. 14, p 1033 (1914).
¶ Rutherford and Richardson, 'Phil Mag,' vol 25, p 722 (1913), and vol 26, p. 324 (1913).
** Barkla, 'Phil. Mag,' vol. 22, p. 396 (1911).

of aluminium   This soft radiation was much more readily absorbed than that emitted by radium B, and for which $\mu = 40$ (cm $^{-1}$), but it was appreciably harder than the characteristic radiation of nickel.   Moreover, when radium C was deposited on silver, little, if any, soft radiation appeared to be emitted.   It seemed of importance, therefore, to examine in detail the nature of the radiation excited by the β- and γ-rays from radium B and radium C, and to examine the bearing of the results on the type of radiation emitted by different materials on which radium C is deposited

Experimental Arrangement

The apparatus used in these experiments was similar to that previously employed in the analysis of the γ-rays   An aluminium electroscope A, which could be filled with the vapour of methyl iodide, was arranged as shown in plan in fig 1   The face B of the electroscope was covered with mica equivalent in stopping power for α-rays to 2 cm. of air   A magnetic field was used in order to prevent the entrance of direct or reflected β-radiation into the electroscope   The pole-pieces of the magnet were 16 cm in length, and in most of the experiments the pole faces were about 9 cm apart   All exposed metallic surfaces were covered with cardboard to reduce, as far as possible, the effect of scattered radiation
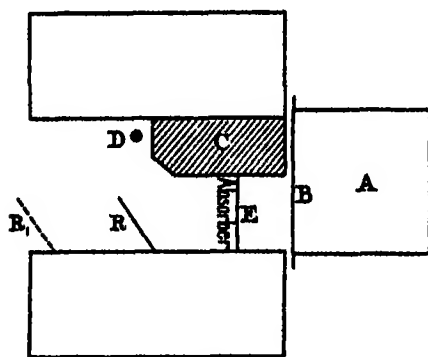
Fig. 1

The active source used throughout these experiments consisted of an α-ray tube containing about 50 millicuries of radium emanation   Such a source, of course, emits a very intense primary γ-radiation, which would be sufficient to mask the effect of any excited radiation produced if suitable means were not adopted to diminish its effect, as far as possible   In order to do this, a block of lead C, 8 cm. long and 4 cm broad, was placed as shown in the figure   The α-ray tube was placed behind this block at the point D   The radiators used throughout were rectangular in shape ($8 \times 3\,5$ cm.), and were, in most cases, sufficiently thick to stop the whole of the β-rays   The radiator was placed, as shown at R, such that the line joining D to the centre of the radiator was parallel to the lines of force of the magnetic field.   Now it is well known that a β-ray projected obliquely to the direction of a uniform magnetic field always moves in a helix whose axis is parallel to the lines of magnetic force.

Consequently, with the particular disposition employed, it will be seen that the β-rays are to a certain extent concentrated on to the radiator Any excited γ-radiation produced may be therefore due either to the impact of the β-rays which strike the radiator, or to the effect of the primary γ-radiation emitted by the radium B and radium C

Method of Experiment

As the method of procedure was practically the same in all cases, it will only be necessary to describe one experiment in detail The radiation from copper was one of the first to be examined This element was selected since one might expect to excite in it a radiation whose effect is relatively very large when methyl iodide vapour is used in the ionisation chamber A copper plate was placed in position at R and readings of the ionisation were taken first of all when no absorbing layers were inserted, and secondly when an aluminium sheet 2 mm thick was inserted at E A large diminution in the ionisation showed at once the presence of a very soft γ-radiation. In order to analyse the radiation which entered the electroscope it was necessary to separate out the effects due to the primary γ-radiation from the source, and which cannot be entirely cut out by the lead block C, and also that due to scattered and reflected radiation To do this it is necessary to take two distinct sets of readings for the ionisation The ionisation is measured for each particular absorbing layer first when the radiator R is in position, and then when the radiator is not present The difference between these two readings gives the ionisation due to any excited radiation together with that due to scattered and reflected radiation Florance[*] in his recent work has shown that the latter is only slightly less penetrating than the primary radiation.

Table I gives the results obtained in one particular experiment with a copper radiator

The curve A, fig 2, shows the results graphically This curve was analysed by the methods already employed in the separation of the γ-radiations It will be seen that in addition to the hard scattered radiation there is also present a soft type which is entirely absorbed by less than 0·5 mm. of aluminium. Curve B shows further that the soft radiation is exponentially absorbed and that it has a mass absorption coefficient in aluminium $\mu/\rho = 47\ 5$ (cm.$^{-1}$). It is clear that this radiation is identical with the characteristic radiation of copper excited by X-rays, for which Barkla found the value of $\mu/\rho = 47\ 7$ The residual radiation is of a much more penetrating

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[*] Florance, 'Phil Mag,' vol. 27, p 225 (1914).

Table I —Copper Radiator

Thickness of aluminium absorber	Ionisation with R in position.	Ionisation with no radiator R	Ionisation due to excited and scattered radiation
mm	divs /min	divs /min	divs /min
0	60 0	34 9	25 1
0 ·0308	52 4	34 8	17 6
0 ·0616	47 ·0	34 8	12 2
0 ·0924	43 4	34 1	9 3
0 123	40 9	33 9	7 ·0
0 185	37 5	33 0	4 5
0 246	36 4	33 0	3 4
0 56	35 8	33 2	2 6
1 12	35 2	32 8	2 4
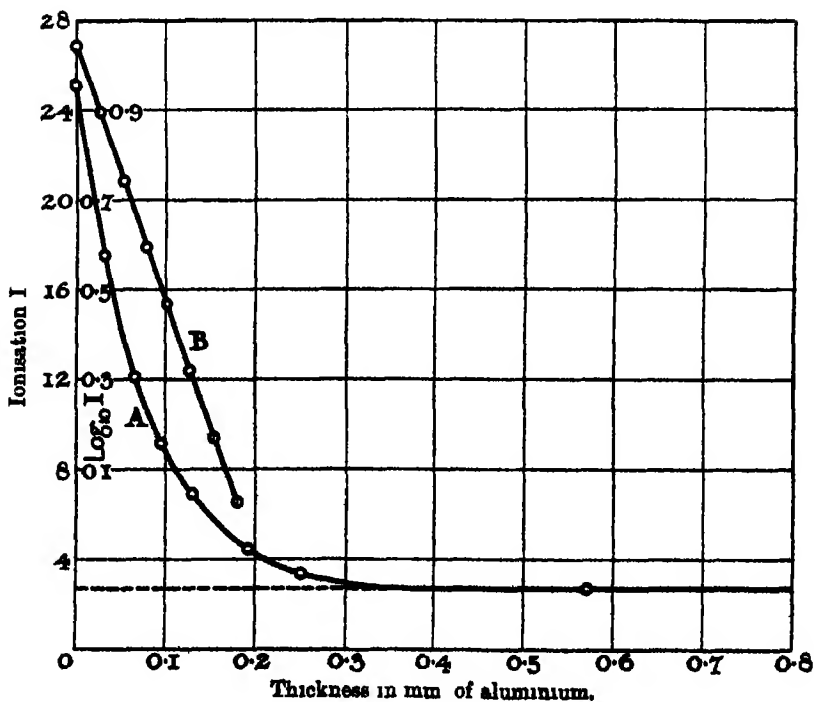
Fig 2

type   It had an absorption coefficient in aluminium of $\mu = 0\cdot2$ (cm.$^{-1}$) and consisted mainly of scattered radiation.

The examination of the excited characteristic radiations has been extended to a large number of elements and compounds.   The following Table gives the results obtained :—

Table II

Element.	Atomic weight	Mass absorption coefficient in aluminium Series K	Mass absorption coefficient in aluminium Series L	Corresponding values of mass absorption coefficients obtained by Barkla and Chapman	
Cobalt	58 9	72 6		71 6	
Nickel	61 6	58 5		59 1	
Copper	63 6	47 5		47 7	
Zinc	65 4	39 8		39 4	
Arsenic	74 9	23 ·0		22 5	
Selenium	79 2	19 3		18 ·9	
Bromine	79 ·9	16 7		16 4	
Molybdenum	96 ·0	4 8		4 7	
Silver	107 9	2 5		2 5	
Tin	119 0	1 6		1 57	
Barium	137 4	0 9		0 8	
Erbium	166 0				
Platinum	195 3		22 8		22 2
Gold	197 2		21 4		21 6
Lead	207 1		17 ·0		17 4
Bismuth	208 0		16 4		16 1
Thorium	232 0		8 5		8 ·0
Uranium	238 0		7 8		7 5

In most cases the pure metals themselves were employed as radiators, but the oxides were used for the examination of the radiations from arsenic, cobalt, erbium, barium, thorium, and uranium, and for that from bromine a thin layer of potassium bromide was taken.   The absorption was in all cases determined in aluminium of density 2 72   The numbers previously obtained by Barkla and Chapman,* for the absorption of the characteristic radiations excited by X-rays are given in the Table   In practically all cases the agreement is very good

It will be seen that the only radiations which it was possible to excite fall into the two groups previously found by Barkla   No evidence has been obtained of a radiation which would correspond to that emitted by radium B and for which $\mu = 0\cdot5$ (cm.$^{-1}$) in aluminium

The question of the relative amounts of radiation excited in each case has not, so far, been examined in detail   Gray† in his early experiments found that the actual amount of excited radiation increased with the atomic weight of the radiator.   As previously pointed out, these results only refer to the penetrating types of radiation excited and do not hold in the case of the characteristic radiations here investigated.   Under the experimental conditions the amount of excited radiation was a maximum for elements of low atomic

* Chapman, 'Roy Soc Proc.,' A, vol. 86, p. 439
† J A. Gray, 'Roy Soc. Proc.,' A, vol. 86, p. 513

weight such as copper, and the amount decreased with increase of atomic weight A comparative idea of the amount of characteristic radiation produced may be obtained by measuring the ionisation both with and without the radiator and comparing the increase in the ionisation for the different radiators Under these conditions in the case of copper the increase was 42 per cent, whereas in the case of barium it was only 9 per cent In considering these results, however, account must be taken of the relative ionisation in the methyl iodide for rays of widely different penetrating power The whole question of the energy of the radiations cannot be conveniently discussed until the absorption of the γ-rays of different types in various gases has been examined. It does not imply, for example, that, because in the case of an element of small atomic weight the ionisation is magnified by means of the methyl iodide vapour, the energy of the characteristic radiation is relatively great This problem is at present under investigation in this laboratory.

Connection of the Results with the Origin of the Characteristic Radiations

Attention has already been drawn to the difficulty of separating entirely the effect due to the β-rays from that due to the γ-rays Several experiments were made in which the α-ray tube was surrounded by different materials, so that advantage might possibly be taken of any difference in the absorbability of the β- and soft γ-rays The difference is not, however, sufficiently great to give any definite results. It will be seen, however, that if the excited radiation is due to the impact of the β-rays and not to the γ-rays, then if the radiator is moved into some position R_1 (see fig 1) the β-rays emitted by the source are no longer concentrated on to the radiator, and the excited radiation should be entirely cut off. Experiments made with varying positions of the radiator showed conclusively that the excited radiations produced are almost entirely due to the impact of the β-rays. It was at first supposed that the excitation of the rays might be due to the γ-rays emitted by radium B and for which $\mu = 40$ This seemed probable, since these soft γ-rays are similar in character to penetrating X-rays used by previous workers for the excitation of characteristic radiations. The results show, however, that any effect due to the γ-rays must be very small compared with that due to the β-rays

It is interesting to note here also that the effect of the α-rays in producing excited γ-radiation must be relatively very small Chadwick first showed that a small amount of γ-radiation is produced when the α-rays of radium C impinge on plates of different material.* The amount of this radiation was,

* J Chadwick, 'Phil Mag,' vol. 25, p. 193 (1913)

however, too small to permit of analysis. In later experiments Russell and Chadwick* distilled polonium on to a copper plate, and were able to detect a very small amount of radiation which appeared to be the characteristic radiation of copper excited by α-rays. In order to examine whether the α-rays from radium C produced any appreciable amount of γ-radiation with the experimental arrangement shown in fig. 1, the ionisation was first of all measured when air was between the source D and the radiator R, the radiator being placed just beyond the range of the α-particles emitted by radium C   A stream of hydrogen was then directed so that the air between D and R was displaced   By this means the range of the α-rays was increased and the rays were able to strike R   No measurable increase of the ionisation was observed, thus showing conclusively that in these experiments the effect of the α-rays is negligible compared with the β-rays in the production of excited γ-radiations.

Experiments with the Penetrating γ-Rays from Radium C

The previous experiments have shown that whilst the β-rays from radium B and radium C excite a large amount of characteristic radiation the γ-rays from radium B do not   Recently Florance† has examined the question of the excitation of γ-rays by the penetrating γ-rays emitted by radium C His experiments would appear to indicate that in one case only, namely, in that of lead, was any such radiation very definitely observed   A slight modification in the arrangement of the above experiment seemed suitable for testing this point. The source used in this experiment consisted, as before, of an α-ray tube containing about 50 millicuries of radium emanation In this case, however, the tube was surrounded by a cylinder of lead 8 mm thick, a thickness sufficiently great to absorb entirely the γ-rays emitted by radium B. In order to reduce the direct effect of the γ-radiation to a minimum, a small pole-piece was used as shown in fig. 3, and the piece of iron which had been removed was replaced by a large block of lead   By this means the direct effect was reduced to a considerable degree. A large radiator R was placed in the position shown, and readings of the ionisation were taken both with and without the radiator, as in the previous experiments. No definite evidence of the production of any excited radiation was observed under the experimental conditions   This was no doubt due to the fact that the amount of radiation excited by the hard γ-rays is relatively much feebler in intensity than that produced by the β-rays. The effects could only therefore be measured by means of a much more sensitive arrangement,

* Russell and Chadwick, 'Phil. Mag.,' vol. 26, p. 113 (1914).
† Florance, 'Phil. Mag.,' vol. 27, p. 225 (1914).
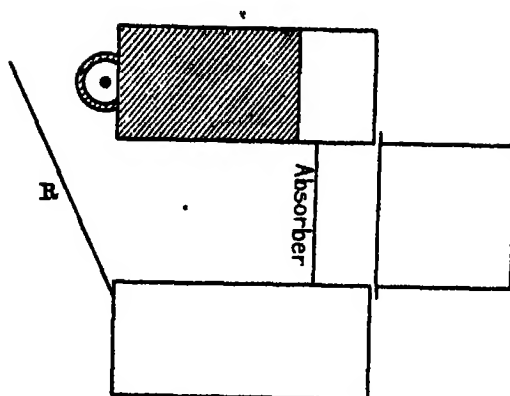
Fig 3

as, for example, by the use of a balance method such as was adopted by Chadwick and Florance

Analysis of the γ-Radiation excited by Radium C in Nickel

The previous experiments show conclusively that the β-rays of radium B and radium C excite the characteristic radiations of those materials on which they impinge   It has already been pointed out that the radiation emitted when radium C is deposited on nickel is not the characteristic radiation of nickel but is appreciably harder   It seemed possible to complete the analysis by depositing radium C on some material, such as aluminium or carbon, which emits a characteristic radiation so easily absorbed that it could not be detected under the experimental conditions.

In order to obtain a deposit of radium C on different materials a very active nickel wire was first obtained by von Lerch's method.   The deposit of radium C was then distilled from the nickel on to the material required. The distillation was carried out in an atmosphere of hydrogen at a temperature of 700° C.   The furnace used for this purpose was the same as that previously used by Russell and Chadwick[*] and described by them in detail The distillation could be quickly and efficiently carried out.

The absorption curve for the γ-radiation emitted when radium C was deposited on a nickel wire was first of all determined   This was found in the usual manner, the electroscope shown in fig. 1 being used, and the lead block C in this case being of course removed.   The curve obtained is shown in fig 4, curve A.   The residual hard radiation due to the radium C is indicated by the dotted line.   A deposit of radium C was then obtained on a thin aluminium strip and the absorption curve for the radiation emitted

[*] Russell and Chadwick, 'Phil Mag.,' vol. 27, p. 112 (1914).
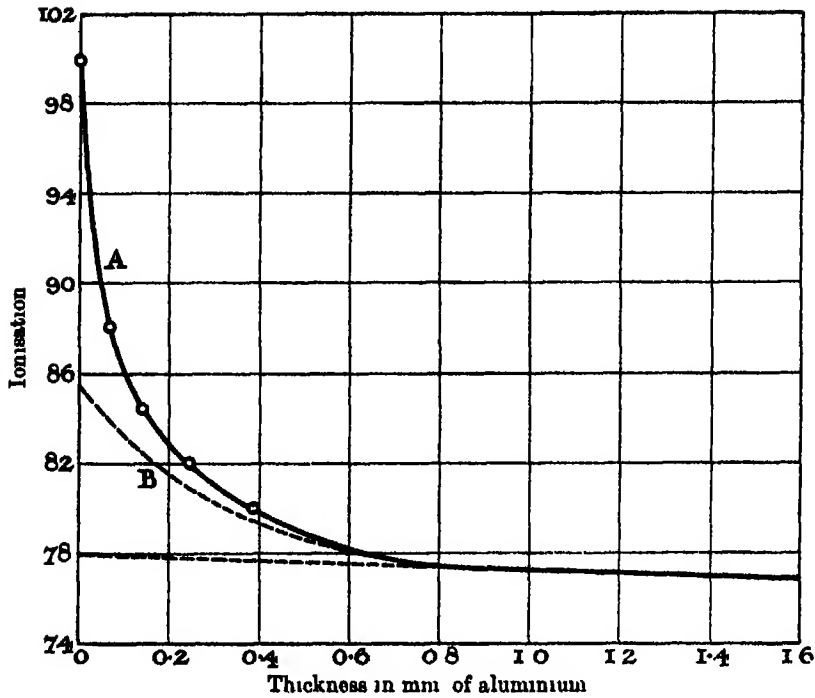
Fig 4.

was found under the same conditions as before   The curve obtained is shown in fig 5   It will be seen from this curve that a small proportion of a soft radiation, amounting to about 7 per cent of the total radiation, is
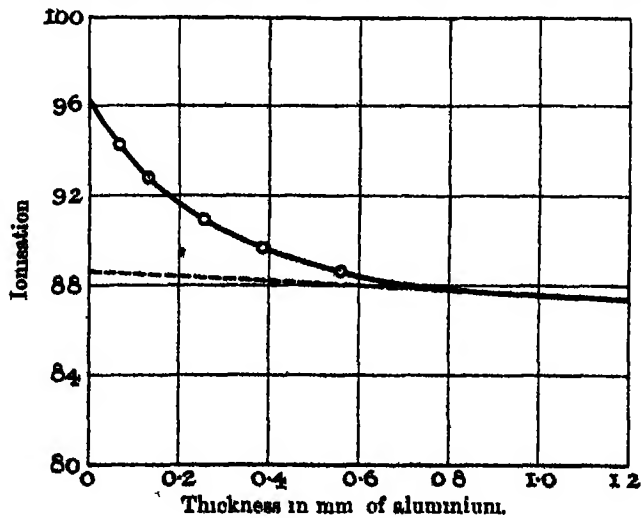
Fig. 5.

given out even when radium C is deposited on aluminium. The analysis of this radiation showed that its absorption coefficient in aluminium is $\mu = 40$, and it is probably identical in character with that emitted by radium B This radiation cannot be excited in the aluminium and would seem to be due to radium C. In order to confirm this conclusion some radium C was distilled on to a thin layer of graphite and the absorption curve was determined as before The curve obtained was identical with that found in the case of radium C deposited on aluminium, the amount of soft radiation emitted being the same in both cases The rate of decay of the active material was in every experiment carefully determined. The results showed that the deposit consisted of pure radium C and did not contain a detectable amount of radium B. This evidence clearly indicates therefore that radium C, in addition to the penetrating radiation for which $\mu = 0\,115$, also emits a small amount of soft radiation for which $\mu = 40$

In attempting to analyse the radiation from nickel it is, of course, necessary to separate the effect due to the soft radiation from the radium C This is easily done since the absorption curves were obtained under exactly the same conditions Fig 4 shows the method of analysis Curve A is the nickel absorption curve and B is the aluminium curve. The difference between the ordinates gives us the effect of the radiation excited in the nickel If these be plotted it is found that the absorption coefficient is the same as that of the characteristic radiation of nickel. Experiments with a deposit of radium C on copper and silver give similar results

Summary

(1) The general nature of the radiations excited when the β- and γ-rays of radium B and radium C impinge on different materials has been examined. Evidence has been obtained which shows that the excitation of characteristic radiations is mainly due to the β-rays and not to the γ-rays

(2) The question of the excitation of characteristic γ-rays by the penetrating γ-rays emitted by radium C has also been examined, but no certain evidence has been obtained of the production of any such radiations.

(3) It has been shown that radium C, in addition to the penetrating type of radiation for which $\mu = 0\,115$, emits also a small amount of soft γ-radiation similar in type to that shown by Rutherford and Richardson to be emitted by radium B and for which $\mu = 40$ in aluminium.

(4) The amount of γ-radiation excited by the α-rays of radium C is negligible compared with that excited by the β-rays.

(5) When radium C is deposited on different materials a soft radiation is

emitted which consists of the characteristic radiation of the material, excited by the β-rays of radium C, together with the soft radiation emitted by radium C.

I wish to express my sincere thanks to Sir Ernest Rutherford for the constant help and valuable advice which he has given to me throughout these experiments

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Electrification of Water by Splashing and Spraying

By J. J NOLAN, M A., M Sc, University College, Dublin

The experiments of Lenard[*] and Sir J J Thomson[†] on the electrification produced by the splashing of pure water and other liquids are well known It was found that distilled water when splashed at a metal obstacle took up a positive charge, giving a negative charge to the air Very dilute solutions of different substances gave very remarkable results, the sign and magnitude of the charge on the liquid depending on the dissolved substance and the degree of concentration of the solution. In all cases the electrification ultimately approached zero as the strength of the solution increased, so that for solutions of quite moderate strength the effect was inappreciable Simpson[‡] has shown that if drops of distilled water are allowed to fall into a vertical jet of air of sufficient velocity, the drops are broken up and acquire a positive charge Investigations of the electrification produced in the air when splashing takes place have been made by Kahler,[§] Aselmann[||] and Simpson. Similar investigations have been made in connection with bubbling and spraying of liquids by Townsend,[¶] Sir J. J. Thomson,[**] Kosters[††], Eve[‡‡] and M Bloch.[§§] A complete account of the subject will be found in a memoir by J J Rey[||||]

[*] Lenard, 'Wied Ann.,' vol 46, p 584 (1892)
[†] J J Thomson, 'Phil. Mag,' vol 37, p 341 (1894)
[‡] Simpson, 'Phil. Trans,' vol. 209, p 379 (1909)
[§] Kahler, 'Ann der Phys,' vol 12, p. 1119 (1903).
[||] Aselmann, 'Ann. der Phys,' vol 19, p 960 (1906).
[¶] Townsend, 'Camb Phil Soc Proc.,' vol. 9, part 5 (1898).
[**] J. J. Thomson, 'Phil. Mag,' p 352 (1902)
[††] Kosters, 'Wied. Ann.,' vol 69, p 12 (1899)
[‡‡] Eve, 'Phil. Mag.,' vol 14 (1907).
[§§] M. Bloch, 'Comptes Rend,' vol. 145, p. 54 (1907).
[||||] Rey, 'Sur l'Ionisation de l'Air par les Chutes d'Eau,' Gauthier-Villars, 1912.

The work described in this paper was undertaken with a view to obtaining some precise data from which it might be possible to establish a connection between the charge produced on the liquid and the extent to which it had been broken up

The liquid used throughout was distilled water, and two methods were employed for breaking it up in contact with air   These were (1) by splashing against an air-blast and (2) by spraying   The experiments made by these methods are described in detail

First Method   Splashing Distilled Water against an Air-Blast

This method resembles that employed by Simpson, but it is more effective and allows the splashed water to be more readily examined. Drops were allowed to fall into a very strong horizontal air-current. Each drop as it entered the air-stream was immediately shattered. A mixture of small drops of different sizes was produced, including a small number of drops of medium size as well as a great number of exceedingly fine drops. These drops were carried forward through different distances by the impetus given by the air-blast, the larger drops being carried farther   A rough sorting-out of the drops into different sizes was thus effected, and it would be possible, by allowing the drops to fall into a vessel set at different points, to compare the charge per cubic centimetre of water for drops of different sizes. Some experiments conducted in this manner showed at once that the charge per cubic centimetre depended on the size of the drops into which the water was broken, the charge being greater as the size of the drops decreased   This method was not, however, found suitable for making accurate measurements of the two quantities concerned.   The drops falling into the receiving vessel at any point were a mixture in varying proportions of drops varying over a considerable range in size   The accidental occurrence of a few large drops would make a very great difference in the results of any measurement   These difficulties were not encountered to such an extent if the receiving vessel was set up immediately under, or only very slightly in advance of the point at which the breaking-up of the water occurs   A rain of fine drops descended from that point without any intermixture of large drops.   The variation of size amongst the drops collected by the receiving vessel in this position was not very serious.   Measurements could therefore be made with a fair degree of accuracy   The size of the drops falling into the receiver could be varied by varying the strength of the air-blast and by varying the height of the dropper. If the strength of the air-current is increased, or if the height from which the water falls is increased, the size of the drops falling into the receiver is diminished.   But we are restricted to a certain small range, for if the air-

current is increased beyond a certain point the spray will be carried forward to such an extent that the residue of fine drops falling into the receiver is insufficient for purposes of experiment. Again it was found that if the height of the dropper was increased beyond a certain point the breaking-up of the drops occurred in such a way as to cause an admixture of large sized drops amongst the fine spray falling into the collecting vessel In spite of these limitations it was found possible to produce a considerable variation in the size of the rain-like spray which fell from the point at which the breaking-up of the water drops occurred. In some cases the receiving vessel was moved forward so as to capture the larger sized drops which had been carried forward some distance by the air-blast. A few successful observations were made in this way, but the risk of error due to the occurrence of large drops is much increased.

The arrangement of apparatus shown in the diagram (fig 1) was adopted
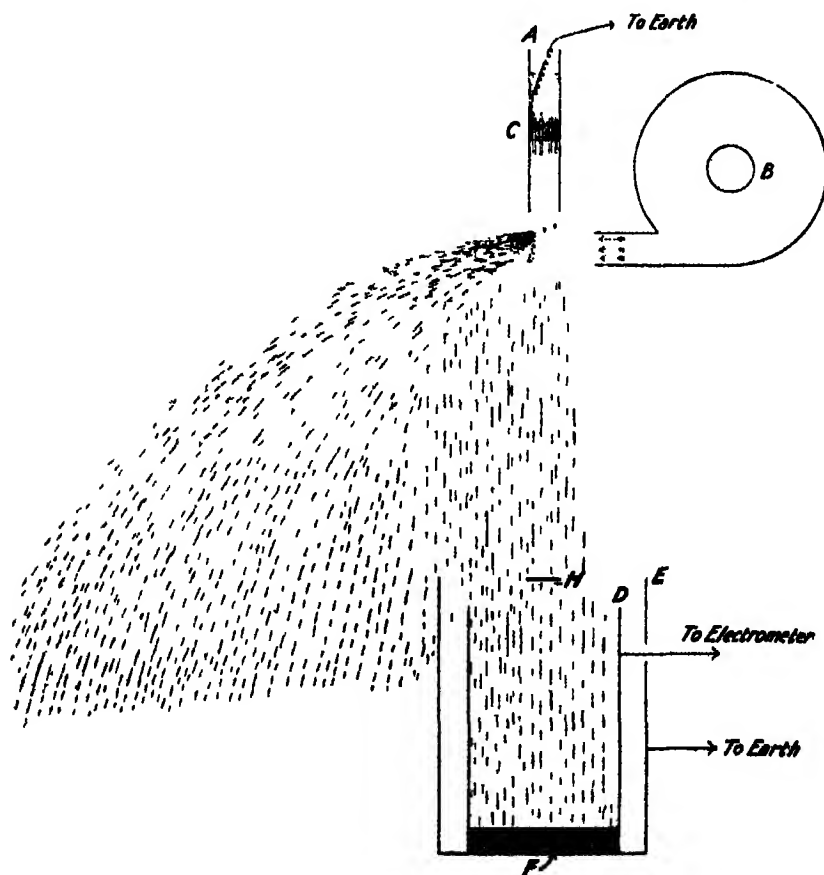
Fig. 1.

B is a Sirocco fan driven by a motor and giving a very strong horizontal
blast of air   A is the water-dropping arrangement.   It is of glass with
a cork at C pierced by 18 short pieces of narrow-bore glass tubing   The
upper part is filled with distilled water, and the whole connected to earth
A rapid succession of drops is thus obtained   The radius of the drops was
approximately 0 25 cm   The receiving vessel D is of cylindrical form,
30 cm in diameter, insulated on paraffin (F) and connected to a Dolezalek
electrometer   It is surrounded by a larger vessel E connected to earth.

It is easy to show that the drops coming away from the dropper are
uncharged (as far as concerns quantities dealt with in these experiments).
When the fan is not acting and the drops consequently fall directly into the
receiver, no appreciable charging occurs.   Furthermore in this case we are
collecting about five hundred times more water per second than when the
fan is acting   When splashing occurs the receiver charges up strongly, and
the charge carried by the drops can be measured very accurately   It is
more difficult to estimate the quantity of water entering the receiver in
any given time and to get a measurement of the size of the drops   The
amount of water was determined by finding the increase in weight of a piece
of blotting paper cut to fit the bottom of the receiving vessel   There is an
error introduced here owing to the evaporation from the blotting paper,
but it was found that if the second weighing was completed rapidly, the
error was not very serious.

We have thus obtained the total weight of water and the amount of charge
which it carried   The next step is to obtain the total number of drops
which have fallen into the receiver   This would enable us to find the size
of each drop   Two points must be considered at this stage, (1) the number
of drops falling into the receiver per second may vary throughout the
experiment, and (2) the number of drops falling per unit area into different
parts of the receiver may be different   Before adopting any counting
method these points must be examined   A ruled surface exposed to the drops
for a certain small time at different stages of the experiment showed that
if any error due to the first cause was present, it was masked by the
ordinary irregularities to which the experiment is subject.   The same
remark applies to observations on the second point   These irregularities,
however, were not so great as to prevent the counting experiments being
made with a fair degree of accuracy.   Two observations were always made,
one at the beginning and one at the end of each experiment, of the number
of drops falling per square centimetre per second into the centre of the
receiver.   Generally, these observations agreed fairly well.   In any case in
which there was a considerable discrepancy the observation was rejected.

The method of procedure adopted in most of the experiments was as follows · The weighed paper was placed in the vessel D and the fan was started. The dropper was filled with distilled water, and the charging-up of the receiver was observed until the dropper was empty   The time during which the water-dropper was acting was noted by means of a stop-watch It was generally about $2\frac{1}{4}$ minutes   The final reading of the electrometer was noted and the paper in D removed and rapidly weighed.   At the beginning and again at the end of the experiment a sheet of metal, 4 cm square, ruled in centimetre squares was introduced at H and exposed for 10 seconds   Owing to the relatively small area of this piece of metal and the shortness of the time for which it was exposed, its introduction did not appreciably affect the amount of water captured by the receiver   It was also easy to verify that its introduction did not affect the rate of charging of the electrometer   The number of drops which had fallen on each square was quickly counted and noted   From the two observations a mean value was obtained from which it was possible to calculate the total number of drops which entered the receiver during the time of the experiment   Hence the mean volume of the drops could be found

The observations taken in one experiment are quoted here so as to give an indication of the magnitudes involved —

Duration of experiment .	$2\frac{1}{4}$ minutes
Electrometer deflection .	143 divisions positive
Capacity of electrometer and vessel	292 cm
Sensibility of electrometer	846 divisions per volt

$$\text{Positive charge received} = \frac{143 \times 292}{300 \times 846} \text{ E S U}$$

$$= 0\,164 \text{ E S U.}$$

Weight of paper (1)	8 743 grm
„ „ (2)	9 015 „

$$\text{Weight of water collected} = 0\,272 \text{ grm}$$

$$\text{Charge per cubic centimetre of water} = \frac{0\,164}{0\,272} \text{ E S U}$$

$$= 0\,60 \text{ E S.U}$$

Mean number of drops per square centimetre in 10 seconds . 3
Area of receiving vessel . . . . 660 sq cm.

$$\text{Volume of each drop} = \frac{0\,272}{3 \times 2\frac{1}{4} \times 6 \times 660} \text{ c c}$$

$$= 102 \times 10^{-7} \text{ c.c}$$

Hence the charge per cubic centimetre corresponding to drops of volume 102×10^{-7} c c is 0 60 E S.U

When suitable conditions were arrived at as regards strength of the air-blast, etc, the drops were generally fairly uniform in size, as could be verified by examining those captured on the ruled metal surface One or two large drops, however, accidentally entering the receiving vessel would vitiate any measurement In many cases this source of error was easily detected on account of the unmistakable marks which the large drops left on the blotting-paper But there is no doubt that it is impossible to be altogether immune from errors of this kind Great difficulty was experienced in obtaining concordant readings of the size of the drops It was hoped that if a great number of experiments were performed, it would be possible to approach a correct result

A great number of the experiments were rejected for various reasons The results which were retained and which are believed to be reliable are set forth in the following Table Many of the numbers given below represent the means of two or more observations, as drops of certain sizes (or very closely approximating to those sizes) tended to recur throughout the experiments ·—

Table 1 —Positive Charge per Cubic Centimetre on Distilled Water broken into Drops of different Sizes.

Charge per cubic centimetre in electrostatic units	Volume of drops	Radius of drops.
	c c	cm
0 54	106×10^{-7}	$13\ 7 \times 10^{-5}$
0 60	102	13 5
0 68	100	13 4
0 79	84 7	12 7
0 80	46	10 3
0 86	50 5	10 6
0 92	20	7 8
0 95	32	9 ·1
1 ·01	18 3	7 5
1 34	8 5	5 ·9
1 36	8 6	5 ·9

An examination of this Table shows that, in spite of certain irregularities, there is a steady increase in the value of the charge per cubic centimetre as the size of the drops gets smaller This is illustrated by plotting the values of the charge per cubic centimetre against the reciprocal of the radius of the drops. In the graph (fig 2), the points obtained from the foregoing Table are shown by the small circles. (The points marked by crosses will be

dealt with later) The points lie roughly about a straight line passing through the origin. This gives us the very simple relation $E = K/r$, where E is the charge per cubic centimetre, r the radius of the drops, and K a constant
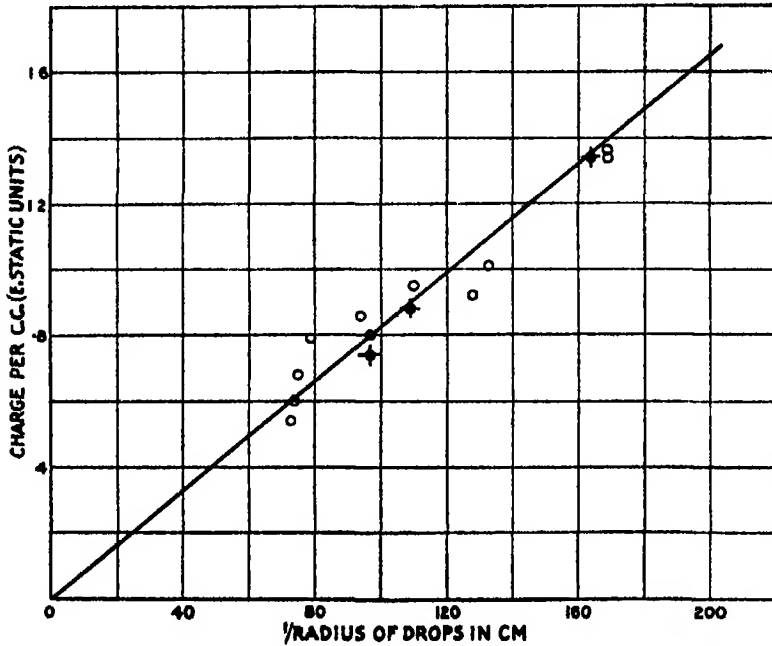
FIG 2

This result is readily interpreted if we make a simple assumption as to the manner in which the water becomes charged. Let us suppose that the charge on the water is proportional to the area of the new water surface created. When a drop of radius R is broken into a great number (n) of small drops of radius r, the increase in surface is

$$4\pi r^2 n - 4\pi R^2$$

Let σ be the charge on the water per unit area of new surface. Then the total charge is

$$4\pi\sigma (r^2 n - R^2)$$

$$E \text{ (charge per cubic centimetre)} = \frac{4\pi\sigma (r^2 n - R^2)}{\frac{4}{3}\pi r^3 n}$$

$$= 3\sigma \left(\frac{1}{r} - \frac{R^2}{r^3 n}\right)$$

$$= 3\sigma \left(\frac{1}{r} - \frac{1}{R}\right)$$

In the experiments described above, R is large compared with r, therefore we may write

$$E = \frac{3\sigma}{r},$$

giving the relation between E and r which has been found experimentally

From the numbers already given we can calculate the value of the constant σ The following Table gives the value of σ calculated for each observation :—

<div align="center">Table II</div>

E in electrostatic units	σ in electrostatic units
0 54	$2\ 46 \times 10^{-3}$
0 60	2 70
0 68	3 04
0 79	3 34
0 80	2 74
0 86	3 04
0·92	2 39
0·95	2 88
1 01	2 52
1 34	2 63
1 36	2 67
Mean value of σ	$2\ 76 \times 10^{-3}$

It will be noticed that there is a considerable variation in the values of σ, the highest being $3\ 34 \times 10^{-3}$ E S U., and the lowest $2\ 39 \times 10^{-3}$ E.S.U   But the agreement is quite as good as could be expected considering the difficulties of the experiment.   It is possible that by some constantly occurring experimental error, the mean value of the constant σ, as determined by these experiments, is erroneous   But there can hardly be any doubt as to the general law expressing the electrical separation that occurs when water is splashed   This may be stated

$$Q = \sigma\, dA,$$

Q being the charge, positive on the water, and dA the increase in area of the water-surface

Second Method   Spraying Distilled Water

In order to test the generality of the result obtained above, another set of experiments was undertaken, using a different method of breaking up the water   Different forms of spraying apparatus were tested, and after some trials an ordinary scent spray was adopted.   When driven by air under pressure, this spray gave a copious supply of water in fine drops.   The size of

the drops could be varied by varying the air pressure. Owing to the large quantities of water given by the sprayer the determination of the charge per unit volume was extremely easy. So great were the electrical quantities involved that in some cases it was necessary to increase the capacity of the electrometer system by 0 2 microfarad. Spurious effects, however, of two kinds have to be guarded against. In the first place, the sprayer has to be well screened against any electrostatic field, otherwise the " water-dropper " effect will occur at the nozzle and the sprayed water will carry away a charge depending in sign and magnitude on the direction and strength of the field In the second place it is possible that the water may become charged by friction against the nozzle   Any effect at the nozzle other than the true air-water effect which we are investigating would give the water a charge of one sign and leave the nozzle with an equal charge of the opposite sign   Consequently if the rate of charging of the nozzle be observed, the charge on the water due to effects of this kind may be allowed for.

The arrangement of the apparatus is shown in Fig 3   The sprayer taken from an ordinary scent-spray is fitted to a vessel containing distilled water The nozzle, which is of brass, is set so that the spray is directed downwards
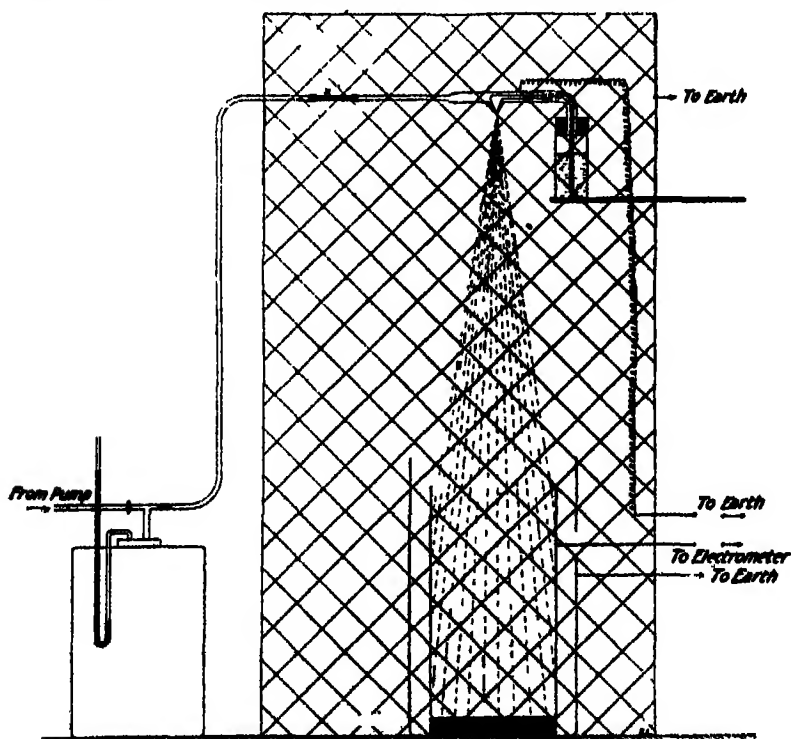
Fig. 3.

The size of the sprayer is much exaggerated in the drawing, the orifice being in reality a mere pin-hole   The sprayer is connected by rubber tubing with the air-supply contained in a reservoir   The pressure in the reservoir is read off by means of a mercury manometer and it can be maintained at any desired value by means of a hand-pump   A length of ebonite tubing is introduced at X.   As the sprayer is insulated from its support, it is thus possible to insulate the spraying system   All the sprayed drops are caught in the receiver, which is set up in the same fashion as in the previous experiments.   An arrangement is introduced by which the receiver and the sprayer can be connected either to earth or to the electrometer   The apparatus is enclosed in a cage of wire netting connected to earth   This excludes the possibility of disturbing electrostatic influences

The method of working is as follows —The pressure is brought to the required value and is kept constant throughout the experiment, usually a few strokes of the hand-pump are sufficient   The sprayer is connected to earth and the charge gained by the receiver per minute observed.   Then the receiver is earthed and the charging of the sprayer observed.   The algebraic sum of the charges gives that part of the charge on the water due to the true air-water effect   The water sprayed per minute is easily measured and the charge per unit volume is at once obtained

The results given below are, in all cases, the means of several experiments

Table III —Charge per Cubic Centimetre on Water sprayed at different Pressures

Pressure	Charge per minute on receiver	Charge per minute on sprayer	Corrected charge per minute on water	Volume of water sprayed per minute	Charge per cubic centimetre (E)
cm Hg	E S U	E S U	E S U.	c c	E S U
7 6	+ 12 4	+ 4 6	+ 17 0	23	0 74
11 6	+ 29 0	− 0 6	+ 28 4	32	0 88
19 6	+ 62 7	− 8 9	+ 53 8	40	1 34

It will be observed that the charge contributed to the water by the sprayer changes sign as the pressure is increased   No detailed investigation of this point was made.

Another set of experiments was now necessary in order to estimate the size of the drops corresponding to different values of E.   The method employed in the previous experiments was adopted, but modifications were necessary owing to the very great number of drops that had to be dealt with.   The sprayer was set up in a closed space so that the spray was

not disturbed by draughts   The spray fell upon a shutter which could be
opened and closed very quickly, exposing a small sheet of silver ruled in
square millimetres   The shutter was connected electrically with a chrono-
graph reading to 1/1000 sec, so that the time for which the shutter was
open was known very accurately   It was generally of the order of
1 second   After an exposure, the sheet of silver was withdrawn and
quickly covered with a watch-glass to prevent evaporation   The number
of drops per square millimetre was counted, a low-power microscope being
sometimes used for this purpose   These measurements gave the number
of drops falling per square centimetre per second   It was only necessary
to set up in the same position a small vessel and weigh the water which
it captured in a known time, in order to have sufficient data to calculate
the average volume per drop

Considerable difficulties were experienced in making these measurements
At first, the number of drops counted per second varied in an irregular
manner   Afterwards, when various devices were adopted to secure
steadiness, this variation was reduced somewhat, but it was difficult to
entirely eliminate it   A great number of experiments were made and the
mean of the results taken   It is believed that the result is fairly correct,
certainly experiments made at different times agree amongst themselves

Results calculated from the best observations are given below

Table IV —Volume and Charge of Sprayed Drops

Pressure	Volume of drops	Radius of drops	E	σ
cm Hg	c c	cm	E S U	F S U
7 6	$46\ 2 \times 10^{-7}$	$10\ 3 \times 10^{-3}$	0 74	$2\ 54 \times 10^{-3}$
11 6	32 5	9 2	0 88	2 70
19 6	9 5	6 1	1 34	2 72

In the last column are given the values of σ calculated as before from the
formula $\sigma = \mathrm{E}r/3$ This formula will hold as in the first experiments,
because here again the original water-surface may be neglected in comparison
with the final area, so that we have

$$\mathrm{E} = \frac{3\sigma}{r},$$

as before.

The agreement with the values of σ obtained by the splashing method is
very striking   The agreement is shown on fig. 2, where the values of E and
$1/r$ by the spraying method are marked by crosses   So good an agreement
between the results of the two methods was, indeed, scarcely to be expected.

In addition to the sources of error in both experiments which have already been referred to, there is a very great difference in the two methods as regards the air which carries the corresponding negative charge   In the first method the negative charge is carried away in the current of air from the fan, and the drops of water on which the charge is measured fall directly out of the air-current.   In the second method the positively charged water and the negatively charged air are blown in the same direction by the sprayer. However, the identity of the constant σ determined by these two methods of experiment can hardly be doubted

Since the value of σ is comparatively high, it should be possible to measure the charge due to small changes in a water-surface.   A number of experiments were attempted with this object   Water was allowed to ascend into a funnel-shaped vessel so that the area of the water-surface was rapidly increasing.   No charge could be detected on the water   A strong current of air was blown over the water-surface while it was changing in area, so as to carry off the negative ions if any were produced.   No difference could be detected.   If a jet of air is set so as to play on a water-surface ripples are produced, but no charging can be detected until the strength and direction of the air-blast are such that the water-surface is broken and drops are carried off in the blast.   The water-surface then takes on a strong positive charge   These experiments indicate that some sort of violent and disruptive action is necessary in order to produce the charge on a water-surface   It would seem as if it were necessary to produce a virgin liquid surface, and that merely to expand an old surface is ineffective.   An account of some experiments somewhat similar to those just described was afterwards found in the memoir of J. J. Rey already referred to   Here, again, it is found that none of the ordinary methods of changing a water-surface will produce an electrical separation

Experiments on Different Liquids.

All the experiments described up to this point were made with distilled water   This was the ordinary distilled water of the laboratory, in the preparation and storage of which no specially high degree of purity is aimed at Ordinary tap-water and some solutions were also examined by the methods of splashing and spraying.   No systematic investigation of either was attempted.   The results obtained harmonise with those of Lenard, Sir J. J. Thomson, and other workers   The Dublin tap-water gives an effect 1/8 or 1/10 that of distilled water   Strong solutions give no charge, weak solutions giving positive or negative values, depending on the solute and the concentration.

Experiments on the Electrification of the Air from the Sprayer.

The air drawn from the sprayer was examined in order to find how the negative charge was carried It is hoped to give a detailed account of these experiments later, when the results are more complete A *résumé* may be given here, however The air was found to contain large numbers of ions of both signs, with, of course, an excess of negative There appears to be present a number of different classes of ions, each class having a definite mobility The values of the mobility vary from that of the ordinary atmospheric ion to that of the large ion discovered by Langevin,[*] and investigated by Pollock[†] and McClelland and Kennedy [‡] Thus the largest ion present has a value for the mobility in a field of 1 volt per centimetre of 0 00035 cm per second approximately This is true for both positive and negative The ion coming next in order of size has a mobility about three times this value. There appears to be no intermediate class Again, at the other end of the scale we find ions of both signs with a mobility of about 1 5 cm per second, apparently identical with the ordinary atmospheric ions There are also present negative ions of mobility 3 cm per second, but no indications of positive ions of that mobility Between the small and the large ions there are groups of ions of various mobilities which have not been fully investigated It is probable that the excess of negative charge on the air is present mainly as small ions, as it is in the number of small ions that the negative charge predominates most markedly

Conclusion

The simple connection demonstrated in this paper between the electrification due to spraying and splashing and the change in area of the liquid surface concerned should help to throw some light on the origin of the electrification in these cases A further investigation of similar effects, and especially a detailed investigation of the nature of the electrification of the air in the different cases, must be completed before an attempt is made to put forward a theory of the effect.

[*] Langevin, 'Comptes Rend.,' vol. 140, p. 232 (1905)

[†] Pollock, 'Le Radium,' vol. 6, p 129 (1909)

[‡] McClelland and Kennedy, 'Roy Irish Acad Proc.,' vol 30, sec. A, p. 72 (1912), and Kennedy, 'Roy. Irish Acad. Proc,' vol. 32, sec A, p. 1 (1913)

The Osmotic Data in Relation to Progressive Hydration.

By W. R. Bousfield, M.A., K.C.

When a concentrated aqueous solution of an electrolyte is gradually diluted there is reason to believe that the amount of water in combination with the solute increases *pari passu* with the ionisation. This progressive hydration must be brought into the account in expressing the conductivity and the osmotic data (in which term we include freezing point and vapour pressure data) in terms of concentration. In a recent paper[*] it was shown that the latest determinations of the osmotic pressures of sucrose solutions by Morse and his co-workers could be simply and accurately expressed in terms of the progressive hydration of the solute. For the correlation of vapour pressure lowering with osmotic pressure, there was used the approximate relation obtained by the consideration of the equilibrium of a vertical column of liquid in contact with the pure solvent through a semi-permeable partition at the bottom and with the vapour of the solvent at the top, which contains as a factor ρ, the mean density of the solution. In the application of the expressions to concentrated solutions of electrolytes it soon became obvious that the presence of ρ, so far from helping the approximation, only threw it out, and the omission of ρ, or rather giving it a constant value unity, gave far more concordant results. In fact the errors introduced by the inclusion of ρ are much greater than the large experimental errors which occur in the measurement of the vapour of even concentrated solutions, whilst the errors when ρ is put equal to unity are considerably less than the experimental errors. The accurate measurement of the osmotic pressures of electrolytes has not yet been achieved, but the theoretical relation between osmotic pressure and vapour pressure forms the connecting link which enables us to express the vapour pressure data for electrolytes in terms of progressive hydration in the simple form

$$\delta p/p = i/(h-n)$$

without any density factor. It is, therefore, important to place the above result on a sound theoretical basis, since it appears to be of wide application in the study of electrolytes. The disappearance of the density factor is really a direct consequence of the relations developed by Callendar,[†] but his development is obscured by the fact that he uses the term "osmotic pressure" in a

[*] 'Trans. Chem. Soc.,' vol. 105, p. 600 (1914).

[†] 'Roy. Soc. Proc.,' vol. 80, p. 466 (1908).

sense which permits its magnitude to vary from point to point of a solution of uniform concentration and temperature   He speaks, for instance, of " the assumption made by Lord Berkeley and Mr Hartley that osmotic pressure varies with concentration only, which appears from their experiments to be approximately true for some solutions"   It was pointed out in a recent communication* that this "assumption" is strictly true for all solutions, if we define osmotic pressure, in accordance with the requirements of the vapour pressure theory, as the liquid pressure under which the internal vapour pressure of the solution becomes equal to the vapour pressure of the pure solvent at the same temperature and under pressure of its own vapour only   From this definition the required relation can be deduced by considering the equilibrium of a small mass of solution of uniform concentration and pressure, instead of a column of solution of varying concentration and pressure.   It may be noted that, at the suggestion of Sir W Ramsay, we avoid the use of the term "hydrostatic pressure," and, in fact, the use of the term is out of place when deriving the relation from the consideration of a small mass of liquid which is mechanically compressed until its internal vapour pressure reaches a certain amount   We have to deal only with the liquid pressure at a point, which is a familiar conception   The idea of the internal vapour pressure at a point within a liquid is not so familiar, but it presents itself, for instance, in the conception of the equality of vapour pressures of ice and water in contact in a state of equilibrium   We may define the internal vapour pressure of a solution at a point as the pressure which would exist within a small sphere permeable only to the vapour of the solvent placed at the point.   This conception brings us into line with the " vapour sieve piston " method by means of which Callendar established the relation

$$U \, dP = v \, dp,$$

where U is " the rate of diminution of volume of the solution at a pressure P per unit of mass of solvent abstracted," and v is the specific volume of the vapour at pressure p

In Callendar's notation the value of U is

$$U = \frac{1}{\rho} - C \, d\left(\frac{1}{\rho}\right) \Big/ dC,$$

where C is the concentration in grammes of solute per gramme of solution Examination of the densities of a number of aqueous solutions shows that we may with an inaccuracy of only about two or three parts per thousand take

$$\frac{1}{\rho} = \frac{1}{\rho_w} - BC,$$

* 'Roy Soc. Proc.,' A, vol. 90, p. 41 (1914).

where ρ_W is the density of the solvent (water) and B is a constant. This gives us $d\left(\dfrac{1}{\rho}\right)/dC = -B$, and therefore

$$U = \cdot 1/\rho_W.$$

That is to say within this limit of accuracy U is simply the specific volume of water The accuracy attained by taking this value of U is considerably beyond that of the experimental vapour pressure determinations which are available *

For the utilisation of Callendar's equation we require to consider the effect of liquid pressure upon U   In the case of dilute solutions near the freezing point, the sensitiveness to pressure of the ice molecules present in large quantities disturbs the regularity of the osmotic pressures, as has been recently pointed out † But in concentrated solutions this difficulty disappears owing to the destruction of ice molecules, and, since U is so closely related to the specific volume of water, we cannot be far wrong in taking for the small variation of U with liquid pressure an expression analogous to that which represents approximately the variation of the specific volume of water with pressure

Let $p_0 =$ vapour pressure of the solution under pressure of its own vapour only,

$p_W =$ vapour pressure of water under pressure of its own vapour only,

$\delta p = p_W - p_0$, the vapour pressure lowering of the solution

$P =$ liquid pressure of the solution,

$U_0 =$ value of U when $P = p_0$.

Then we may say $\qquad U = U_0[1 - \beta(P - p_0)]$,

or, since the magnitude of β is of the order 0 00005, we may for the purpose of integration conveniently take

$$U = U_0[1 + \beta(P - p_0)]^{-1}.$$

We may also, within the desired limits of accuracy, take for the relation between the pressure and specific volume of saturated water vapour

$$v = R'T/p.$$

Substituting these values for U and v in the equation

$$U\,dP = v\,dp,$$

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* For instance, in the extreme case of 40-per-cent. lithium chloride solution, the value of U is 0·996, which only differs from the value of U for an "infinitely dilute" solution by 1 part in 200 The error in the vapour pressure lowering determined experimentally is not less than 1 in 100

† 'Roy Soc. Proc.,' A, vol. 90, p. 45 (1914).

and integrating at constant temperature, we get

$$\frac{U_0}{\beta} \log\left[1 + \beta(P - p_0)\right] = R'T \log(p/p_0)$$

The integration constant is obtained from the consideration that the liquid pressure in the solution when under pressure of its own vapour only is p_0, that is to say, when $p = p_0$ we must have also $P = p_0$ The above equation expresses the relation between liquid pressure P and internal vapour pressure p As the liquid is compressed by varying pressures P the internal vapour pressure p is changed in accordance with the above expression   But it is essential to clearness of ideas not to regard any value of P as "osmotic pressure" except the particular value which P must have in order to make $p = p_W$ Thus we get for the osmotic pressure in accordance with our definition

$$\log\left[1 + \beta(P - p_0)\right] = \frac{\beta R'T}{U_0} \log(p_W/p_0),$$

where P now stands for the osmotic pressure of the solution at absolute temperature T

Putting $\delta p = p_W - p_0$, expanding the logarithms, neglecting small quantities of the second order and neglecting also p_0 in comparison with P on the left-hand side we obtain the equation

$$\frac{P}{R'T} = \frac{1}{U_0} \cdot \frac{\delta p}{p_W},$$

which has already been obtained by Callendar, Porter and others   The point of the deduction set out above is that the expression is deduced from the strict definition of osmotic pressure, which does not permit us to regard osmotic pressure as varying with "hydrostatic pressure."

Since within the limits of experimental error of vapour pressure determinations we can put $U_0 = 1$, the expressions formerly given for the osmotic data in terms of progressive hydration* can now be put in the simpler and yet more accurate form,

$$\frac{P}{R'T} = \frac{\Delta}{F'} = \frac{\delta p}{p} = \frac{\imath}{h - n}$$

Here P is the osmotic pressure expressed in atmospheres, Δ is the freezing point depression of the solution, $\delta p/p$ is the ratio of the vapour pressure lowering to the vapour pressure of water at the same temperature, h is the total number of molecules of water to one molecule of solute, n is the number of molecules of water in combination with one molecule of the solute, and $\imath$ is the ionisation factor, the best values of the constants being $R' = 4557$ and $F' = 103\cdot6$.

* 'Trans. Chem. Soc.,' vol 105, p 609 (1914).

As an illustration of the practical value of the relations thus formulated we may refer to a paper written concurrently with the present communication,* in which it is shown by their use that the dilution law $a^2/(1-a)= K(h-n)^3$ is valid for the chlorides of lithium, sodium and potassium both in dilute and in concentrated solutions and that it is in conformity with the requirements of the law of mass action.   There is reason to believe that the simple relation $\delta p/p = \imath/(h-n)$ which it is the purpose of the present communication to establish is even more accurate than the approximations by which it is reached would lead us to expect, and that the small inaccuracies introduced by the approximations practically cancel one another, except in the region of dilute solutions near the freezing point, in which the idiosyncrasies of water are so marked   But here the relation is never in practice required, since the values of δp are so small as to be incapable of direct measurement

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On the Origin of the Electron Emission from Glowing Solids

By Frank Horton, Sc D

(Abstract)

The electron emission from Nernst filaments has been measured under different conditions and the following results have been obtained —

1. The electron emission from a filament heated by an alternating current is of the same magnitude as that obtained when the filament is heated by a continuous current to the same temperature.

2. The electron emission from a Nernst filament at a given temperature is the same when heated by conducting an electric current as when heated by a glowing metal wire passing through it.

3 The electron emission from a Nernst filament heated in the usual manner is the same as that given by the material of the filament when powdered and heated upon platinum.

These results show that the action of an oxide cathode does not depend

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upon electrolysis accompanying the conduction of a current through the oxide.

Various suggestions as to the origin of the electron emission from glowing solids are discussed in the paper, and it is concluded that the experimental evidence points to the correctness of the original theory that an electron emission can arise as a result of thermal agitation alone, but that this emission may be aided or hindered in several ways.

Attempts to Produce the Rare Gases by Electric Discharge.

By Thomas R. Merton, B Sc (Oxon)

The object of the present investigation was to obtain some further evidence on the apparent production of 'neon and helium by electric discharges in vacuum tubes, which has been described by Collie and Patterson *

Strutt† has recently attempted to repeat these experiments, using methods somewhat different to those of Collie and Patterson, with negative results

It is evident that in experiments of this kind the most rigorous precautions must be taken to exclude air from the apparatus, for although the rare gases are only present in the atmosphere in relatively small quantities, an exceedingly small quantity of air is required to give evidence of their presence. Strutt (*loc cit*) has been able to detect with his apparatus the neon in 0 01 c.c. of air and has expressed the opinion that under favourable conditions the neon might be detected in 0·001 c.c.

The method of the present investigation differs essentially from that used either by Collie and Patterson or by Strutt.

The apparatus, shown in the figure, consists of a bulb A connected to a glass tube L, which passes very nearly to the bottom of the bulb B. From the tube L are two branch tubes C and D, of which C leads to the sparking tube S and palladium tube P, and D leads to the stopcock H and thence to the mercury pump. The tube D is connected by a bye-pass E, with a stopcock, to the bulb B, which is provided with another branch tube with a stopcock F. At the top of the bulb A is a fine capillary tube K, into which is sealed a fine

* 'Trans. Chem. Soc,' vol. 103, p. 419 (1913).
† 'Proc. Roy. Soc.,' A, vol. 89, p 499 (1914).

platinum wire.   There is also a platinum wire sealed into the tube L.   P is a short length of palladium tube soldered with gold to a platinum tube, which
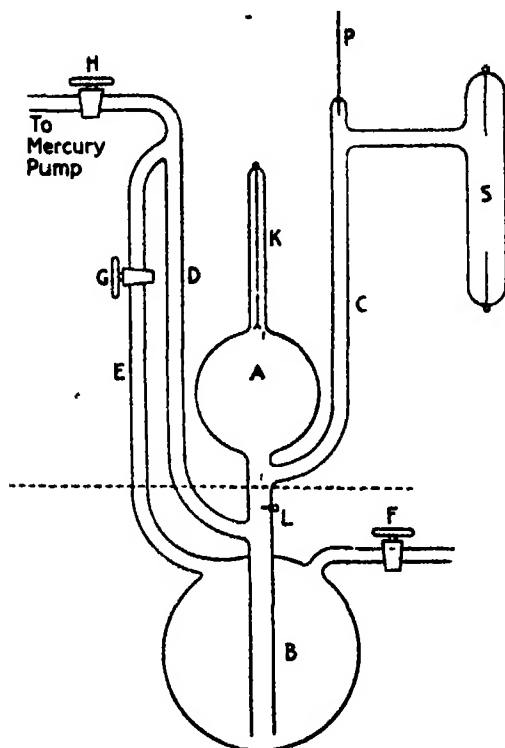
is in turn sealed into the glass tube C.   The sparking tube S was provided with stout electrodes fastened to platinum wires and sealed into the tube in the usual way.

The experiments were conducted as follows: The bulb B was nearly filled with mercury.   Taps G and H were opened and F was closed, and the apparatus was exhausted by the mercury pump until no discharge could be passed through the sparking tube S.   During this process, a heavy discharge from a ten-inch induction coil was passed through the tube, which was also heated at intervals with a bunsen burner.

Hydrogen was admitted by heating the palladium tube P in a bunsen flame, and the hydrogen so admitted was pumped off.   This process of admitting and pumping off hydrogen was frequently repeated in order to wash any traces of other gases completely from the apparatus.   Stopcocks G and H were then closed and air was cautiously admitted into the bulb B until the mercury stood at the level shown by the dotted line in the figure.   A and S

were thus completely protected from any possible leakage from the stopcocks by the mercury seal

A moderately heavy discharge from the induction coil was then passed through the sparking tube, hydrogen being admitted through the palladium tube at intervals when the vacuum became too high

After the conclusion of the sparking the hydrogen remaining in the apparatus was almost completely removed by heating the palladium tube by means of a small spiral of platinum wire maintained at a red heat by an electric current   This operation presumably reduced the pressure of hydrogen in the apparatus to the partial pressure of hydrogen in the atmosphere. During this process the sparking tube, which was usually coated with a dense metallic mirror from the electrodes, was frequently heated   The gas remaining in the bulb A was then driven into the capillary by slowly admitting air into the bulb B through the stopcock F, and examined spectroscopically by passing a weak discharge from the induction coil through the platinum wire in the capillary, connection to the mercury being made through the wire at L

Before the commencement of the sparking, the absence of atmospheric contamination could be shown by driving the gas in the bulb A into the capillary and examining it spectroscopically   In the first four experiments moderately heavy discharges were passed through the sparking tubes, which were provided with aluminium electrodes, for periods of from six to fourteen hours.

The residual gases in these experiments showed, after the sparking, only lines due to mercury with a trace of hydrogen and sometimes a trace of carbon The latter was rapidly absorbed by the mercury when the discharge was passed   An experiment in which the electrodes were of platinum and another in which the sparking tube contained a globule of mercury, also gave negative results.

In the next two experiments aluminium electrodes were used and the discharge from the coil was rectified by inserting a spark gap in the circuit, consisting of a fine point and a flat metal plate, the latter being connected to the negative pole of the coil, the experiments being in other respects conducted in exactly the same manner.   In these two experiments the residual gases showed the spectrum of argon.   No trace of nitrogen was found.

Three more experiments were conducted without the rectifier and in no case was any argon found.   In the next experiment a valve tube rectifier was substituted for the spark gap which had been previously used, and a trace of argon was again found.

The experiments thus far seemed to indicate that, whatever might be the source of the argon, a rectified discharge was essential to its appearance, but

numerous subsequent experiments have shown that there is no systematic connection between the character of the discharge and the appearance of the argon in the residual gases.

Two experiments were carried out to discover whether the argon could be traced to the gases liberated from the electrodes. In one experiment the electrodes were only sparked for a short time during the process of pumping and washing out the tube, and at the conclusion of the experiment a trace of argon was found   In the second experiment no discharge was passed until the pumping and washing out was concluded   A large quantity of gas was liberated from the electrodes on sparking and was rapidly absorbed by the aluminium mirror, but no argon was found.

In both of these experiments the discharge was rectified with the valve tube, and it is concluded that the argon cannot be traced to the gases liberated from the electrodes. An experiment was conducted in which the washing out of the apparatus with hydrogen was omitted. A trace of air therefore remained in the apparatus. At the conclusion of the experiment no nitrogen, oxygen or argon were found.

Both the diatomic gases and the argon had evidently been absorbed by the electrodes or the aluminium mirror and the amount of argon driven off on heating the tube was too small to detect. A similar experiment in which the sparking was only continued for about twenty minutes, so that no appreciable aluminium mirror had formed, gave a distinct argon spectrum, with no nitrogen.

It follows from these two experiments that the presence of argon in the residual gases cannot be explained by the presence of a minute quantity of air remaining in the apparatus if the sparking is continued for a considerable time   The presence of the argon, however, can be accounted for by an exceedingly small, but continuous leak, since the diatomic gases appear to be far more rapidly absorbed by the aluminium mirror than the argon.

With the apparatus used a minute continuous leak can occur under certain circumstances. It was found that a small amount of dirt had collected on the tube L which constitutes the barometric seal. A new apparatus was, therefore, taken and carefully cleaned with fuming nitric acid, and the mercury, which had been purified by passage in a fine stream through dilute nitric acid, was poured into the apparatus without coming into contact with any tap grease.

Since these precautions were adopted, no trace of argon has been found after an electric discharge had been passed in the manner described above; many experiments have been made with electrodes of aluminium, copper, nickel, silver, platinum and palladium, and all have given negative results. In some experiments an air trap was inserted in the tube L as an additional

precaution, but it seems as if this is unnecessary if the mercury and glass are scrupulously clean   In order to test whether the appearance of argon could occur through a slow leak of air into the apparatus through stopcocks, three experiments have been carried out in which the mercury was not driven up to the level of the dotted line in the figure, the vacuum being maintained by the stopcocks.   These stopcocks gave every appearance of being reliable, but in two cases out of the three a trace of argon was found.

The spectroscopic test of argon appears to be more delicate than that of neon, and it follows therefore, from Strutt's (*loc cit*) estimate for neon, and from the fact that there is about a thousand times as much argon as neon in the atmosphere, that a millionth of a cubic centimetre of air might be sufficient for the detection of argon

From the above experiments it is considered doubtful whether stopcocks can be relied on in dealing with quantities of gas of that order of magnitude.

These experiments seem to suggest that the appearance of argon should be treated as an exceedingly delicate test for a leak in the apparatus, and the entire results of the investigation have therefore been negative, since in the numerous experiments under different conditions in which no argon has been found, no trace of neon or helium has been observed   It must be pointed out that both Collie and Patterson (*loc. cit*) and Strutt (*loc cit*) removed the diatomic impurities in the residual gases by means of charcoal cooled with liquid air, a process which would also have removed any argon present.   In the present investigation, it is highly probable that in those experiments in which argon was found in sufficient quantity, the neon and helium would have been detected if the argon had been removed in this way.

It must, however, be remembered that the leak of air which can be revealed by argon is exceedingly small, and about one thousandth of the quantity which could be detected if the test used were that of the recognition of neon, and that therefore the presence of recognisable quantities of neon, and more particularly of helium, would indicate a leak greater than it appears possible to attribute to the inefficiency of stopcocks.

Note on the Paper by T. R. Merton on " Attempts to Produce the Rare Gases by Electric Discharge "

By J Norman Collie, F R S

The apparatus used by Mr Merton in the above-mentioned paper was very kindly handed over to the author   The following experiments were made with it ·—Five grammes of metallic uranium were finely powdered in a steel·mortar and then heated to redness in a water-pump vacuum for half an hour   The metal was then transferred to a small bulb in which the metal could be bombarded with the cathode discharge, and this tube sealed on to the Merton apparatus.   A small bulb containing charcoal, a hard glass tube containing copper and copper oxide, and a small bulb with phosphorus pentoxide were also sealed on to the apparatus   The whole was then pumped out and washed out several times with oxygen till the spark would not pass in the tube containing the uranium   The tube was then heated as strongly as possible and the gases pumped off and examined , carbon gases and hydrogen were present, but only just enough helium and neon to detect them in the ordinary way using a capillary tube   The tube was again washed out with oxygen and pumped till the spark would not pass through the tube containing the uranium   The palladium tube was then heated for about 20–30 seconds so as to admit hydrogen and allow the spark to pass   The bombardment of the uranium lasted about two hours.   During all this time carbon gases and hydrogen were evolved from the metal   These were absorbed by keeping the charcoal bulb cooled in liquid air and heating the copper oxide   At the end of *Experiment* 1 enough helium and neon at about 2 mm. pressure remained to fill the capillary examining tube and also a small space below

Experiment 2.—Bombardment for one and a-half hours.   Rather less helium and neon   (The helium lines—red, yellow, and green—not so strong as in Experiment 1)

Experiment 3 —Bombardment for one and a-half hours , same result as in Experiment 2 , the capillary tube filled with neon and helium.

Experiment 4.—Bombardment one and a-half hours.   After the experiment the charcoal bulb was heated and the copper oxide tube also heated, and only the phosphorus pentoxide tube cooled   Other gases than carbon dioxide and water vapour would therefore not be condensed.   The uncondensed gases in the capillary tube gave the nitrogen spectrum ; after the

nitrogen had been got rid of by sparking above the mercury, the whole capillary, as before, was left full of neon and helium, and just enough argon to show the blue spectrum   In this experiment and all the following ones, before beginning the bombardment of the uranium, mercury was run up to the top of the capillary, showing that no gases remained in the apparatus from the former experiment

Experiment 5 —Bombardment one and a-half hours   Result the same as in Experiment 4, but by continual. sparking to get rid of the nitrogen (nitrogen combines with the mercury under these conditions) the capillary tube pitted round the platinum electrode and finally cracked.

Experiment 6 —A new bulb and new capillary tube were sealed on to the apparatus, which was carefully heated and washed out with pure oxygen till on running up the mercury into the capillary all gas disappeared on sparking   After the bombardment of one and a-half hours was over, before taking the charcoal out of the liquid air the mercury was run up to the capillary and the usual amount (namely, the whole of the capillary) of neon and helium was found. The charcoal was then taken out of the liquid air and heated and the copper oxide tube heated, and the phosphorus pentoxide tube cooled in liquid air   The remaining gases, as before, now consisted of neon, helium and nitrogen, with just enough argon to show (after the nitrogen had been removed by sparking), but the volume was the same as when only neon and helium were in the capillary tube.

Experiment 7 —Bombardment one and a-half hours. The result was exactly similar to the preceding experiment

Experiment 8 —A repetition of No 7, with the same result.

Experiment 9.—In all the former experiments a coil giving a 10-inch spark with a platinum break was used   A bigger coil with a mercury break was now employed   The bombardment was for one and a-half hours   Neither neon nor helium could be detected in the residual gases.

Experiment 10 —The old coil with the platinum break was again used , before, however, the residual nitrogen could be got rid of by sparking through the capillary tube, pitting occurred and the tube broke.

Experiment 11 —A new capillary tube was sealed on, and after an hour's sparking with the old coil neon, helium, nitrogen, and a trace of argon were found as before.

In all the above experiments the charcoal was strongly heated between each experiment and the apparatus washed out with oxygen made by heating permanganate of potash in a tube sealed on to apparatus. The pump employed always held a green phosphorescent vacuum from day to day.

During all these experiments the gases in the tube were entirely cut off

from the stopcocks during the whole of the experiment   Moreover, if the neon and helium found were due to an air leak, it is difficult to account for the disappearance of the argon, which should have been present to the extent of one thousand times as much as the neon and helium found.   The amount of argon present, however, was too little to be measured, as it made no difference in the volume of the neon and helium (*cp* Experiments 6, 7, and 8)   The presence of the nitrogen is probably due to a nitride of uranium   The author, however, has only been experimenting with the apparatus for less than a month, and in work of this sort experiments must be repeated more than once before reliance can be placed on them , but that comparatively large amounts of neon and helium should come off from uranium by bombardment with the cathode rays, and not by heating, is a matter of interest , also that in one experiment a change of coil should affect the result is an observation that must if possible be repeated.

That the presence of neon and helium in vacuum tubes, after the electric discharge has been passed, is due to an air leak seems most improbable Where the gases come from has yet to be proved   They have been found by Sir J. J. Thomson, by Sir W. Ramsay, by Mr G. Winchester,[*] and by the author, Mr. Patterson, and Mr Masson   Mr. Winchester is of the opinion that they are in some way occluded in the metal of the electrodes, and are not disintegration products of other elements   Whatever the source may be, it is only by further experiments that the question will be solved   The author hopes shortly to publish a more detailed report on the work done on this subject in conjunction with Mr. Patterson and Mr Masson.   He also wishes to thank Mr. Merton for the most useful apparatus with which the experiments were made.

The Capacity for Heat of Metals at Low Temperatures

By E H. Griffiths, Sc D , F R S , and Ezer Griffiths, M.Sc , Fellow of the University of Wales

(Abstract)

In the first part of the paper of which this is an abstract, an account is given of the apparatus and the method employed in determining the atomic heats of the metals Na, Al, Fe, Zn, Ag, Cd, and Pb, at various points in the range from 0° to about −160° C

A new method of maintaining an enclosure for long periods at any desired temperature within this range is described, the Joule-Thomson cooling effect of air on expansion being utilised for this purpose

Details of the method of controlling the temperature are given , here it suffices to say that there was little difficulty in keeping the oscillations in temperature of the exterior walls of the copper enclosure within a hundredth of a degree in magnitude

In the case of sodium special experimental difficulties presented themselves, and the internal portion of the apparatus differed in design from that used with the other metals   The platinum thermometer was in the centre of the block, while the heating coil, consisting of insulated manganin wire enclosed in fine metal tubing, was distributed throughout the mass of the metal   This form of heating coil promises to be of considerable service in the investigation of poor conductors of heat

We may remark that the method employed in this investigation, although differing in fundamental respects from the one used in the previous work,[*] gave values which closely confirmed those results where the temperature ranges overlapped

A study of the observations of Nernst on the metals silver and lead has led us to the conclusion that no difference, greater than the probable error of experiment, exists between the values given by his method (electrical) and those obtained in our own investigations   Hence, for the metals Al, Cu, Zn, Ag, and Pb, it is possible to extend the atomic heat curves through the observations of Nernst at liquid air and hydrogen temperatures.

The only data available, at very low temperatures, for Na, Cd, and Fe are those of Dewar at about 50° Abs   But, for reasons given in the paper, we

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[*] 'Phil. Trans.,' A, 800, vol. 213, p. 119 (1913).

are unable to attach to the absolute values obtained by Dewar's method the same weight as to those of Nernst

In Table I the values of the atomic heats are given at convenient intervals of temperature, so as to facilitate the testing of any theory over an extended range. These values have been obtained from smoothed curves drawn through our observations from 400° to 120° Abs, and extended through the observations of Nernst or Dewar above mentioned

Table I.

Aluminium

T (Abs)	32 4	80	120	200	250	300	340	380		
C_p	0 25	2 27	3 74	5 14	5 54	5 81	5 98	6 13		

Iron

T		50	110	150	210	250	310	350	390	
C_p		0 98	3 47	4 50	5 36	5 70	6 09	6 28	6 41	

Copper

T	23 5	50	90	130	170	210	250	290	390	
C_p	0 22	1 32	3 48	4 78	5 23	5 50	5 70	5 83	6 09	

Zinc

T	30	80	120	160	210	250	310	350	390	
C_p	0 94	4 09	5 15	5 61	5 82	5 95	6 10	6 19	6 25	

Silver

T	35	60	100	150	200	260	300	340	380	
C_p	1 58	3 32	4 83	5 55	5 83	5 98	6 05	6 12	6 21	

Cadmium

T	50	100	140	200	260	300	340	380		
C_p	3 46	5 37	5 79	5 99	6 14	6 24	6 33	6 44		

Lead.

T	23	37	50	80	100	140	200	300	380	
C_p	2 96	4 50	5 14	5 72	5 87	5 97	6 10	6 32	6 49	

Sodium

T	50	90	150	240	300	330	360	368	373	393	413
C_p	3 50	5 04	5 90	6 36	6 66	6 85	7 33	7 48	7 44	7 39	7 34

In the second part of the paper a brief review is given of the various formulæ which have been proposed for the representation of the atomic heat.

Einstein's theory, based on the conception of the atoms as consisting of a number of Planck's resonators with a single frequency, gives values which are too small at low temperatures.

Nernst and Lindemann's formula, which is an empirical modification of Einstein's expression, taking into account two frequencies, the one the octave of the other, gives values which are, in general, too high at low temperatures

Debye has given a solution of the general case in which there is a continuous series of frequencies from zero to a certain limiting value characteristic of the substance   The value of this limit frequency can be calculated from the elastic constants   His theory is based on a number of hypotheses which cannot be accepted as being strictly valid, but of the formulæ hitherto published for the representation of the atomic heat curves of the metals, that of Debye gives the closest approximation to the experimental results.

The following three examples show the order of agreement between the observed and the calculated values, and it will be observed that the discrepancies exceed the possible errors of experiment

Temperature	C_p (observed)	C_p (calculated)	Difference
	Aluminium		
°			
35	0 33	0 35	−0 ·02
80	2 27	2 33	−0 ·06
140	4 26	4 26	
200	5 14	5 10	+0 04
250	5 53	5 47	+0 06
300	5 81	5 74	+0 07
350	6 13	6 01	+0 12
	Silver		
35	1 58	1 64	−0 06
85	4 42	4 53	−0 11
120	5 20	5 21	−0 01
200	5 84	5 78	+0 06
280	6 ·01	6 01	
360	6 16	6 15	+0 ·01
	Lead		
23	2 ·96	2 95	+0 ·01
80	5 72	5 64	+0 ·08
120	5 ·98	5 91	+0 ·02
200	6 10	6 13	−0 03
280	6 28	6 28	
360	6 45	6 45	

Of the metals considered in the paper, lead has the lowest frequency and aluminium the highest   In the comparison above given, the limit frequency inserted in Debye's formula is such that the calculated value coincides with the observed value at about 120° Abs, this being the lowest temperature to which we carried our investigation.

The elastic constants of the metals are in some cases so discordant that

the calculated values of the frequencies can only be regarded as confirmatory of the value inserted in the atomic heat formulæ

The following comparison shows the order of agreement between the values obtained by the two methods :—

$$V_m \times 10^{-12}$$

Metal	Al	Ag	Pb
V_m (specific heat)	8 0	4 8	1 9
V_m (elastic constants)	8 8	4 4	1 5

Prof Callendar has kindly inserted a note regarding his theory of atomic heat

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Dilute Solutions of Aluminium in Gold

By C T Heycock, F R S, and F H Neville, F R.S

(From the Goldsmiths' Metallurgical Laboratory, Cambridge)

(Abstract)

The paper deals with the solid condition of alloys containing not more than 5 per cent by weight of aluminium   The diagram is a concentration-temperature diagram, the atomic percentage of aluminium being measured horizontally from left to right, and the temperature, in degrees Centigrade, being measured vertically

The alloys melt at varying temperatures, but below the upper line *Aabcd* of the diagram they are wholly solid , we may say, approximately, that they are wholly solid below 525° C   Between this temperature and the level of the point L there is a range of 100°.   The diagram shows four compartments in this area and records the following facts :—The first area, on the left, indicates the fact that gold can dissolve rather more than 2 per cent by weight of aluminium to form uniform solid solutions; these we call *α*.   With rather more aluminium we have the complex alloys of the second area, containing, in addition to *α*, a second constituent *β*.   In the alloys of the third compartment, *β* is the sole constituent, while in the fourth a new

constituent D appears Like *α*, *β* can vary in composition, but only between narrow limits, D is probably the compound Au₅Al₂.

The solid *β* may be regarded as a solvent for *α* and D, for when the
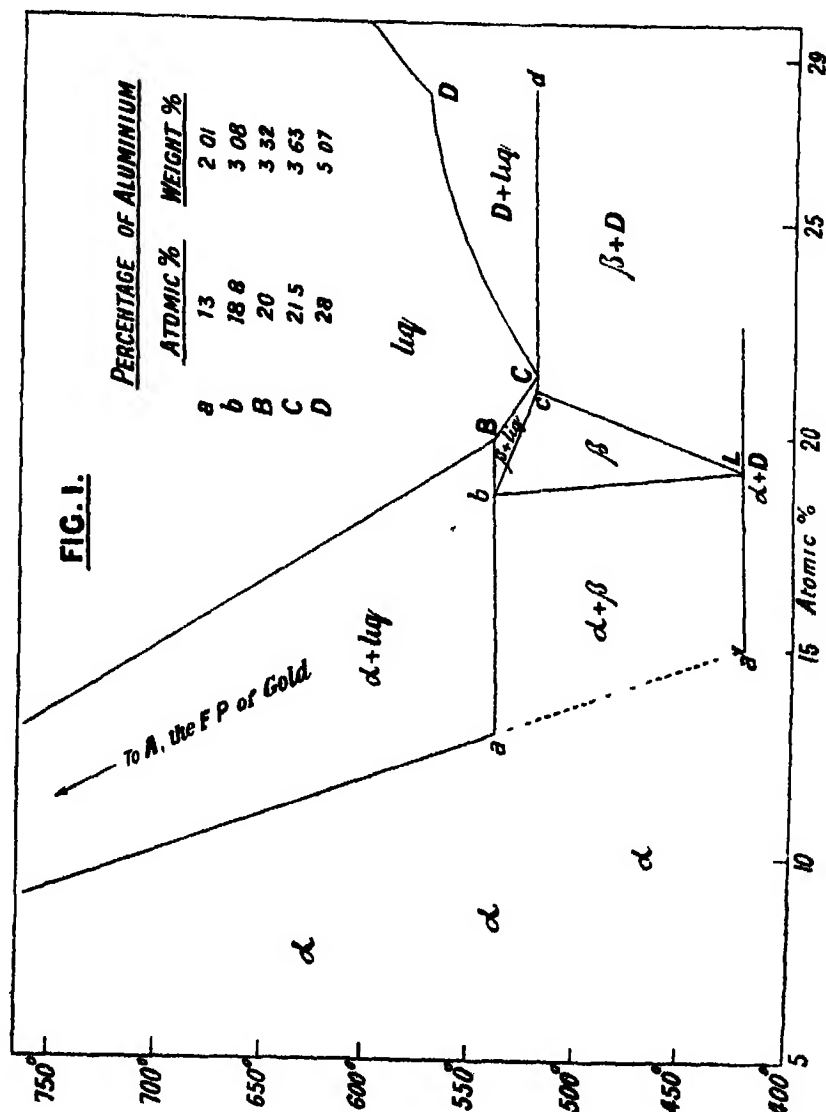
representative point of an alloy passes, by cooling, out of the triangle *bLc*, then *α* or D crystallises from the previously uniform substance of the alloy, the form in which the D crystallises being somewhat remarkable. L is an eutectoid point, when a slowly cooled alloy falls below 524°, the

temperature of the L point, the residual β breaks up into a "pearlite" or eutectoid complex of α and D, the β-phase wholly disappearing

The above remarks apply only to alloys that have been cooled from the molten state to temperatures not below 400° C. If cooled below 400°, the alloys with an aluminium content between 2 and 5 per cent. by weight undergo a remarkable change, they recalesce, the temperature suddenly jumping as much as 70° in the case of alloys containing 3 3 per cent. by weight of aluminium, with a smaller rise in the case of alloys with a greater or less percentage   The microscope shows that the recalescence is due to a decomposition, or recrystallisation, of the β, or more precisely, to a reaction between the α and the D of the L eutectoid   The recalescence causes a permanent change in structure that is unaffected by prolonged annealing at any temperature below 520°, so that the new state must be regarded as the stable one at all temperatures below 520°   The recalescence sometimes, but rarely, occurs spontaneously above 410°, but between 2 5 and 4 per cent of aluminium it can be provoked at much higher temperatures, for example, if an ingot near L in composition be cooled from the molten state, and at 500°, or even as high as 514° (where it is wholly solid), it be touched with a cold steel wire, the recalescence occurs with a rise of temperature to near 525°, but never to above this point. A complete recrystallisation takes place, with partial fusion of the ingot   Such a profound change caused in this way is somewhat remarkable.

We have strong reason to think that, in all cases of recalescence, the new substance formed is the definite compound Au_4Al The diagram we give does not apply to the alloys containing the new substance.

On the Convection of Heat from Small Cylinders in a Stream of Fluid : Determination of the Convection Constants of Small Platinum Wires, with Applications to Hot-Wire Anemometry.

By Louis Vessot King, B A. (Cantab.), Assistant Professor of Physics, McGill University, Montreal

(Abstract.)

Part I

Sections 1 *and* 2.—Until comparatively recently, the problem of solving the equations of heat conduction in the case of a solid cooled by a stream of fluid had received little attention, although the general problem was formulated by Fourier* himself as long ago as 1820   In 1901 the problem was taken up by Boussinesq,† and many cases were dealt with in his memoir of 1905. By means of an extremely elegant transformation Boussinesq was able to express the general equation for the two-dimensional problem in a linear form by transforming the equation to the set of orthogonal curvilinear co-ordinates determined by the stream-lines and equipotentials of the hydrodynamical problem of the flow of a uniform stream of velocity V past the cylindrical obstacle, the equation for the temperature θ at any point of the fluid takes the form

$$\partial^2\theta/\partial\alpha^2 + \partial^2\theta/\partial\beta^2 = 2n\partial\theta/\partial\beta, \tag{1}$$

where the curves $\alpha = constant$ represent the stream-lines and $\beta = constant$ the equipotentials. The constant n is given by the relation $2n = cV/\kappa = s\sigma V/\kappa$, where c is the specific heat of the fluid per unit volume, s that per unit mass, σ its density, and κ its thermal conductivity   If the surface of the cylinder be the particular stream-line $\alpha = 0$, and the critical equipotentials be the curves $\beta = 0$ and $\beta = \beta_0$, the heat-flux per unit length of the cylinder is given by

$$H = -\int_0^{\beta_0} \kappa (\partial\theta/\partial\alpha)_0 \, d\beta, \tag{2}$$

where the integral is taken to include the two branches of the stream-line $\alpha = 0$.

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* Fourier, 'Mémoires de l'Académie,' vol 12, p. 507 (1820)

† Boussinesq, 'Comptes Rendus,' vol. 133, p 257 , also 'Journ. de Mathématiques,' vol. 1, pp. 285–332 (1905).

The transformation just described reduces the problem for any cylinder to that of calculating the temperature distribution in a uniform stream flowing parallel to the axis of $x (a = 0)$ when the temperature or the heat-flux is prescribed over the interval $x = 0$ to $x = \beta_0$. Boussinesq obtains an approximate expression for the heat-loss by neglecting the term $\partial^2\theta/\partial\beta^2$ in equation (1), and deriving a simple Fourier solution corresponding to the condition that the temperature be constant over the cylindrical boundary *

Section 3 —It was found by the writer that Boussinesq's result did not meet the requirements of the experiments on the convection of heat from small platinum wires cooled by a stream of air   The complete formulation of the possible boundary conditions is most conveniently obtained by expressing the problem in terms of an integral equation.   Use is made of H A Wilson's solution† for the temperature at any point (x, y) due to a line source of strength Q at the origin in a stream of fluid flowing parallel to the x-axis in the form

$$\theta = (Q/2\pi\kappa)e^{nx}K_0(nr), \tag{3}$$

where $K_0(z)$ is that solution of Bessel's equation most conveniently defined by the definite integral

$$K_0(z) = \int_0^\infty e^{-z\cosh\phi}\,d\phi \tag{4}$$

If $u(\xi)\,d\xi$ represent the total flux of heat from an elementary portion $d\xi$ of the x-axis between $x = 0$ and $x = \beta_0$, the boundary condition over the axis $y = 0$ is expressed by the relation

$$2\pi\kappa\,\theta(x) = \int_0^{\beta_0}u(\xi)\,e^{n(x-\xi)}K_0|n(x-\xi)|\,d\xi, \tag{5}$$

where $\theta(x)$ is the temperature at the point $(x, 0)$ of the boundary.   If the temperature is prescribed over the boundary, (5) constitutes an integral equation for the determination of $u(\xi)$, if the flux of heat $u(\xi)$ is prescribed over the boundary, the same equation gives the temperature of the stream in contact with the boundary.   In either case, the total heat-loss from the cylinder per unit length is given by

$$H = \int_0^{\beta_0}u(\xi)\,d\xi. \tag{6}$$

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* Boussinesq's expression for the heat-loss per unit length from a cylinder of radius a is given by $H = 8\sqrt{(s\sigma\kappa Va/\pi)}\,\theta_0$, where θ_0 is the excess of temperature of the cylinder above that of the fluid at a distance

† H. A. Wilson, "On the Convection of Heat," 'Camb Phil. Soc. Proc.,' vol. 12, p. 406 (1904)

Sections 4–7.—A solution of equation (5) in which the heat-flux is assumed to be constant over the boundary gives rise to an expression for the heat-loss which is in good agreement with the results of experiment on the convection of heat from small platinum wires cooled by a stream of air In this case the heat-loss per unit length is given by the equation

$$H = 2\pi\kappa\theta_0 n\beta_0 \Big/ \Big[\int_0^{x_0} e^u K_0(u)\,du\Big]. \tag{7}$$

In order to test the theory, it is necessary to tabulate the function $\int_0^x e^u K_0(u)\,du$. Use is made of the tabulated values of the function $K_0(x)$,* and the integral is evaluated step by step by making use of Euler's formula for quadratures, the arithmetical operations being easily carried out by means of a calculating machine The graph of the function $y = x\Big/\Big[\int_0^x e^u K_0(u)\,du\Big]$ plotted against $\sqrt{x}$ is shown in the accompanying figure Over the range
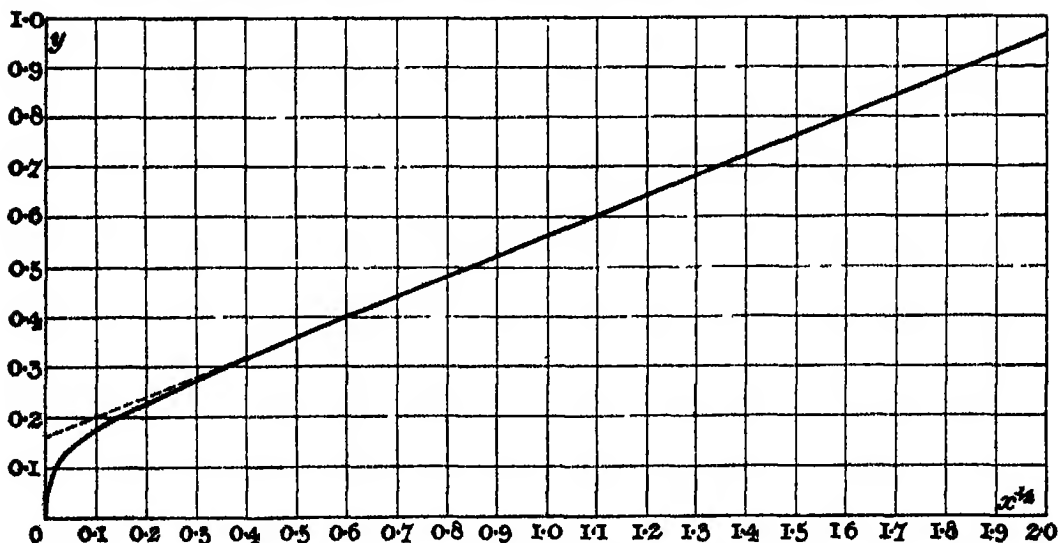
of values of the variable corresponding to the interpretation of the experiments on the convection of heat, the curve lies extremely close to its asymptote

$$y = 1/(2\pi) + \sqrt{[x/(2\pi)]}, \tag{8}$$

while for small values of the variable it can easily be shown that an approximate value is given by

$$y = 1/[(1-\gamma) - \log\tfrac{1}{2}x], \tag{9}$$

* Tables due to W. S. Aldis ('Roy. Soc Proc,' vol. 64, p. 219 (1896)) are given by Jahnke and Emde, 'Funktionentafeln,' p. 135 (Teubners, 1909).

γ being Euler's constant, $\gamma = 0.5771$. The corresponding expressions for the heat-loss per unit length for a cylindrical wire of radius a are :—

(High velocities) $H = \kappa\theta_0 + 2\sqrt{(\pi\kappa s\sigma a)}\, V^{\frac{1}{2}}\theta_0,$ (10)

(Low velocities) $H = 2\pi\kappa\theta_0/(\log b/a),$ (11)

where b in (11) is given by $b = \kappa e^{1-\gamma}/(s\sigma V)$

The boundary condition of constant flux gives rise to a discontinuity of temperature over the boundary, from the point of view of the kinetic theory of gases, temperature conditions cannot be strictly defined in the immediate neighbourhood of the heated cylinder, and it is only at a distance of several free paths when equi-partition is nearly complete that temperature can strictly be defined and that normal thermal conduction takes place. Equation (10) gives so good an account of the experiments that it seems possible to make use of the method of flow in a determination of the thermal conductivity of gases, the form of apparatus required lends itself easily to measurements over a wide range of temperature and pressure   The kinetic theory offers some support as to the condition of constant flux being very approximately physically realised in the case of a stream of gas moving over a thin wire, should this prove to be the case, the somewhat indeterminate boundary conditions in the statical methods of measuring thermal conductivity would be avoided.

Part II—Experimental

Sections 8 and 9—The present experimental investigation was undertaken with two objects in view —

(1) To study the laws of the convection of heat from small platinum wires heated by an electric current over as wide as possible a range of temperature, air-velocity and diameter in the light of the theoretical development of Part I, and to obtain in absolute measure the convection constants of small platinum wires.

(2) To make use of the constants thus obtained in the design of accurate and portable wind-measuring apparatus to form the basis of a standard system of anemometry, as well as to serve for use in a great variety of engineering and aerotechnical problems.

The general arrangement of apparatus necessary to carry out the requisite measurements of heat-losses from a series of platinum wires of diameters 1 to 6 mils consisted of a rotating arm capable of adjustment to any speed as calculated from a chronograph record.   At various lengths along this arm could be clamped a light fork designed to hold the specimens of wire under test.   The latter formed part of a Kelvin double bridge, electrical connection being obtained through a central mercury connecting switch and overhead

wires to the remainder of the bridge. By means of a rheostat it was possible at each speed to adjust a measured current through the wire so as to bring its resistance to a value corresponding to a pre-determined temperature In this way it was possible to vary at will the various factors of temperature, air-velocity, and heat-loss

In order to obtain a correct measurement of velocity by the use of a rotating arm, it was found necessary to make a correction for the velocity of the vortex set up in the laboratory This was accomplished by making use of one of the wires previously tested on the rotating arm as a hot-wire anemometer for measuring the velocity of the vortex set up by the rotating arm, for a wire fixed at any radius it was found that the velocity V relative to the air of the room is connected with the velocity V_r relative to the room itself by the relation $V = (1-s) V_r$, s being a constant for the radius employed and the disposition of the apparatus in the room The constant s may be conveniently called the "*swirl*" and expressed in percentages of the apparent velocity, for a radius of 2 6 metres s is as much as 5 per cent

Sections 10 *and* 11 —The wires employed were drawn down through diamond dies from a length of 6 mil pure platinum wire whose constants were accurately known for the purposes of platinum thermometry It was found necessary to redetermine the temperature coefficients after each wire had been heated for a considerable time to about 1200° C in the course of the convection experiments The diameters of the 10 sizes of wire tested (from 6 to 1 mil) were directly measured to within 1 per cent. by means of a high-power microscope

Section 12 —Under conditions of rapid cooling by convection, the calcula-tion of the temperatures of the wire from its resistance may be subject to uncertainties due to the existence of gradients of temperature. It is shown that under extreme conditions the excess of temperature of the centre of the wire over that of the boundary cannot exceed 0 6° C at 1000° C, so that this source of error is negligible More serious is the cooling effect of the leads and potential terminals, which must be so arranged that this source of error may be within the limits of experimental errors, the effect is calculated out in detail and a numerical table is drawn up showing that with the disposition of apparatus of the convection measurements the error due to the leads and potential terminals may be neglected. The possibility of error becomes more serious in the design of hot-wire anemometers with short wires, and in any particular case may be kept within small limits by a reference to the above-mentioned Table. The importance of keeping the anemometer wire from vibration is shown by a mathematical investigation of the error involved.

Section 13.—Observations on the heat-loss per unit length from a series of

ten platinum wires of diameters 6 to 1 mil under varying conditions of temperature and wind-velocity are analysed in detail. For each velocity (corrected for " *swirl* ") the currents required to heat the wire to a pre-determined series of resistances (from which the temperatures were calculated) were measured The corresponding heat-loss in watts per unit length was calculated for each temperature the theory of Part I suggests that the results be examined in the light of the formula $W = B\sqrt{V} + C$, where B and C are functions of the temperature and of the dimensions of the wire When W is plotted against $\sqrt{V}$ for each temperature, a family of straight lines is obtained and by determining the line of closest fit to the observed points, the constants B and C can be found for each wire

It is found by plotting B against $\theta - \theta_0$, the excess of temperature of the wire above the surrounding air, that the resulting graph approximates very closely to a straight line for a range of temperature attaining to as high as 1200° C. this result may be expressed by the relation $B = \beta(\theta - \theta_0)$, where β shows the existence of a small temperature coefficient represented by $\beta = \beta_0[1 + b(\theta - \theta_0)]$, b having the value $b = 0\ 00008$ Finally theory requires that β_0 be proportional to $\sqrt{a_0}$, a_0 being the radius of the wire A graph of β_0^2 against a_0 shows this condition to be satisfied, leading to the final result

$$\beta_0/\sqrt{a_0} = 1\cdot432 \times 10^{-3} \quad \text{(experimental)} \tag{12}$$

The theoretical formula (10) requires

$$\beta_0/\sqrt{a_0} = 2\sqrt{(\pi s_0 \sigma_0 \kappa_0)} = 1\ 66 \times 10^{-3} \quad \text{(theoretical)}, \tag{13}$$

taking $\sigma_0 = 0\ 001293$, $\kappa_0 = 5\ 66 \times 10^{-5}$ calorie and $s_0 = 0\ 171$ calorie The agreement of (12) and (13) must be considered fair in view of the uncertainty attached to the value of the thermal conductivity for air, and also in the fact that the theoretical investigation does not take into account the variation of this and other factors with the temperature gradient in the neighbourhood of the wire

In order to interpret the constant C in terms of formula (10), it is necessary to calculate the contribution to the term C due to radiation It is shown from the observations of Lummer and Kurlbaum[*] that the radiation loss from polished platinum at absolute temperature Θ° C is given in watts per cm.² by the relation

$$e = 0\ 514(\Theta/1000)^{5\ 2}. \tag{14}$$

Having calculated the radiation loss per centimetre of the wire from the formula $E = 2\pi a\ e$, we obtain the true convection loss $C_0 = C - E$. it is found for each wire that C_0 is very nearly proportional to the temperature difference

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[*] Lummer and Kurlbaum, 'Verh. Deut. Phys. Ges., Berlin,' vol. 17, p. 106 (1898).

$\theta - \theta_0$, and may be represented by the formula $C_0 = \gamma_0(\theta - \theta_0)[1 + c(\theta - \theta_0)]$, γ_0 being nearly independent of the diameter of the wire and having the value

$$\gamma_0 = 2\ 50 \times 10^{-4}(1 + 70a) \quad \text{(experimental)} \tag{15}$$

According to the theoretical equation (10), $C_0 = \kappa_0(\theta - \theta_0)$, giving

$$\gamma_0 = \kappa_0 = 2\ 37 \times 10^{-4} \text{ watts} \quad \text{(theoretical)}, \tag{16}$$

in excellent agreement with the observed value (15) The coefficient c has the value $c = 0\ 00114$, which may be considered to represent in large measure the variation of the heat conductivity with the temperature

Section 14 —It was found that the constant β_0 varied in a marked manner with the inclination of the wire to the direction of the stream, an effect which can be utilised in practical anemometry in determining the direction of the resultant flow in a complicated distribution of air-velocity

Section 15 —Formula (11) for small velocities agrees in form with the empirical formula proposed by Langmuir* to represent the results of his experiments on the free convection of heat from small platinum wires The corresponding mathematical problem has not yet been solved completely, but may be dealt with in the light of the present investigation by supposing that the wire is cooled by a current of effective velocity V due to the ascent of heated air over the surface of the cylinder Making use of the constants obtained from the present experiments on forced convection, Langmuir's observations can be interpreted and the velocity of the "effective" convection current estimated, these results are of some importance in hot-wire anemometry as the "effective" velocity sets a lower limit to value of the air-velocities which it is possible to measure by this means.

Part III

Sections 16–18 —The special type of portable hot-wire anemometer developed by the writer may be called a linear anemometer in contradistinction to several forms of integrating instruments which have already been described.† Detailed specifications are given for the construction of such anemometers The Kelvin bridge connections are retained, and this makes it possible to make use of previously calibrated anemometer wires A 3-mil platinum wire, heated to about 1000° C, was found to be the most convenient in practice , by means of a portable galvanometer the current required to bring the resistance of the anemometer wire to about

* Langmuir, "Conduction and Convection of Heat in Gases," 'Physical Review,' vol. 34, p. 415 (1912)

† Bordoni, U., 'Nuovo Cimento,' Series VI, vol 3, pp. 241–282, April, 1912 , Morris, J. T., 'Engineer,' September 27, 1912 , 'Electrician,' October 4, 1912, p 1056 , Gerdien, H., 'Ver Deut. Phys. Ges.,' No 20, 1913

four times its resistance at room temperature is measured. For the same wire the current i required to bring the wire to the prescribed resistance and temperature in a current of air of velocity V is given by a relation of the form

$$i^2 = i_0^2 + k\sqrt{V}, \qquad (17)$$

i_0^2 and k being the constants of the instrument determined either by calculation or by direct calibration   Experiments carried out by Prof A M Gray* and the writer indicate that consistent measurements of turbulent flow and of sharp gradients may be obtained independently of the diameter of the wire   It was found possible to resolve a gradient in which the velocity changed by 5 cm /sec over a distance of 1/10 mm

The advantages of the anemometer designs and connections described may be briefly stated as follows.—

(i) The use of the Kelvin bridge connections makes it possible to standardise and calibrate anemometer wires at a central laboratory independently of the remainder of the apparatus with which the wire is to be employed

(ii) These connections also enable the wire to be heated to a high temperature, with the result that the determinations of velocity are practically independent of ordinary variations of room temperature

(iii) The use of the linear anemometer makes it possible to establish a consistent measure of turbulent flow

(iv) The linear anemometer makes it possible to analyse sharp gradients of velocities without disturbing the flow at the point of measurement

(v) The properties of the Kelvin bridge connections make it possible to connect an anemometer through low-resistance slip rings, and provide a means of attacking such problems as the analysis of velocities in the neighbourhood of rapidly revolving aeroplane propeller blades, or between the blades of centrifugal fans.

An instrument of the type described could easily be constructed to give a continuous graphical record, thereby greatly increasing its usefulness in the analysis of complicated velocity distributions

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On Some Sources of Disturbance of the Normal Atmospheric Potential Gradient.

By W. A Douglas Rudge

The author has made a study of some of the abnormal variations due to local circumstances and it appears that there are three main factors besides rain, hail and snow which may exert a disturbing influence, viz —

1 The presence of dust raised by the wind sweeping over loose soil, etc., or by traffic passing along roads and streets.

2 The presence of dust produced during certain manufacturing operations

3 The presence of clouds of steam

1. *The Effects due to Dust*

In various communications[*] it has been shown that the presence of dust had a very marked influence on the atmospheric potential gradient, and in the earlier work it seemed to be in the direction of reducing the gradient or changing its sign from + to —, the magnitude of the change depending upon the amount of dust present in the air These observations were taken in Africa and were carried on during a period of nearly four years over a large tract of country which included such places as Cape Town, Bloemfontein, Kimberley, Johannesburg, Pretoria, Durban, Lourenço Marques, Victoria Falls, Beira, Zanzibar, Mombasa, Port Sudan, Suez, Cairo, Port Said, and at altitudes varying from sea-level up to 7000 feet As far as Africa is concerned, the general result was that in nearly every case the presence of dust, whether raised by the wind or by trains, camels, horses or motor cars, caused the positive potential gradient to be diminished, and in extreme cases reversed During a "dust" storm negative potential gradients of 10,000 volts ([1]) per metre were not infrequent, but the positive value was as a rule quickly restored after the dust had settled The curve A (fig 1) is a record of such a storm taken with a Bendorff electrometer, the positive values of the gradient being shown above the line OO', and the negative values below ; the normal fine weather curve (B) is shown for contrast. The sensitiveness of the electrometer was such that it could not record greater value than 400 volts per metre, and the horizontal portions of the curve indicate that the gradient was too high—

* 'Roy. Soc South Africa,' vol 2, Part V (1912) ; 'Nature,' March 13, 1913 , 'Phil Mag.,' April, 1913 ; 'South African Journ. of Science,' February and March, 1912

probably over 2000 volts per metre—to be recorded.   In addition to the
negative charge given to the air a positive charge was present upon the dust
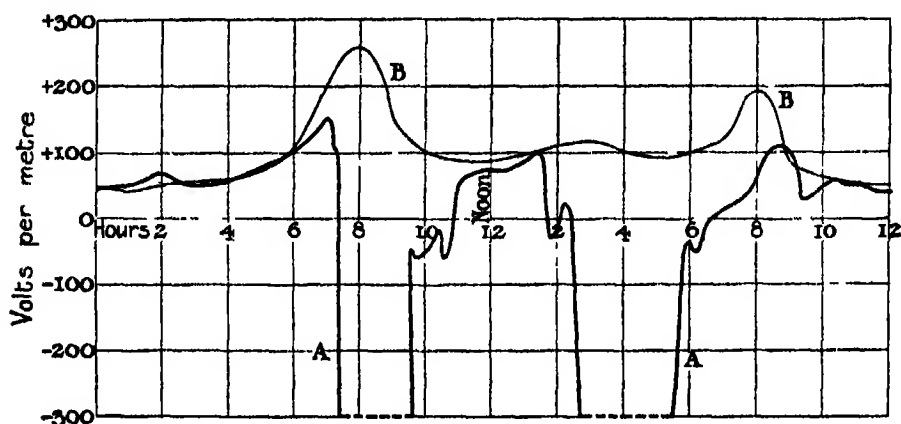
Fig 1

when it was of a siliceous character , but an extensive series of experiments
made with dusts of different natures show that some give negative charges to
the air, and others positive charges   The negative charge seems to be
associated with those bodies of an "acidic" character, whilst the positive
charges are given by those of a "basic" character, or by salts such as the
carbonates in which the acid is weak *

In order to observe the effect of dust upon the potential gradient any form
of electroscope furnished with a radium-coated wire to act as a collector will
suffice   A small pocket electroscope, which can be attached to a walking-
stick, has been used for making qualitative tests, but for quantitative work
the Wulf electrometer is very convenient   Perhaps a radium-coated wire
is not the best form of collector if absolute values are required , but for
comparative tests it is unsurpassable   On exposing the electroscope, say,
on the roadside or in a street, the radium collector rapidly takes up the
potential of the air in its neighbourhood, and the leaf remains steady for
some little time , but if, however, a cloud of dust is raised by any means
the potential will alter, increasing or diminishing, or even reversing in
sign, according to the nature of the dust raised   It has been mentioned
that the charge upon the dust is opposite in sign to that upon the air,
and this has been seen in a most striking fashion.   During a strong South
African dust-storm it was observed that an electroscope placed near to a
window occasionally showed a divergence of its gold leaves which at first was

* 'Phil. Mag ,' April, 1913.

attributed to air currents, but the effect was really due to the air inside the room becoming charged, as the following experiment shows. The window was raised for some distance and a piece of wood fitted in to fill up the gap. A hole about 20 cm in diameter was made in the wood and a tin tube fitted in, but well insulated by means of several layers of paraffined paper; the end of the tube projecting into the room was covered with a piece of wire gauze and several layers of fine chiffon. The dust blown in through the tube charged it so strongly with *positive* electricity that sparks could be obtained from it, and at the same time charged up the air of the room with *negative* to such an extent that an electroscope furnished with a radium collector indicated a charge in any part of the room, in some parts sending out the leaf to a right angle.

In taking observations in Europe one is generally confined to the dust which can be raised by the wind or by the passing of motor cars, etc, over roads. The surface of the country is not dry enough, as a rule, to permit of a cloud of dust being raised from the ground by the wind, but in some instances, ploughing after harvest has yielded sufficient dust to make its influence felt. Galloping horses on the sea shore, well above high-water mark, raise a sufficient cloud of dust to reverse the positive potential.

Observations have been taken at many places in Europe, in cities and along country roads, and the changes in the potential qualitatively observed. The effect of a dust composed entirely of siliceous materials, such as sand, weathered granite, basalt, fine clay, etc, is to diminish or, in extreme cases, to reverse the positive potential, whilst that of a calcareous material is to increase the positive potential. If there is a mixture of materials there is generally an increase of the positive potential, and on all old roads there is, in addition to the stony material, a large amount of organic matter, so that the general effect of dust is to cause the potential to increase. The actual change in the value of the gradient may be very large, say, from 100 to 500 volts per metre, the effect is, however, transient, and disappears with the settling of the dust. Upon freshly repaired sandy roads in Cambridgeshire and the New Forest, passing motor cars raised clouds of dust which gave a negative potential, but after a few days' use, sufficient organic matter accumulated to cause the normal positive potential to be increased.

Since most roads are "metalled" with siliceous materials, the charge given to the air might have been expected to be negative,[*] but certainly on old roads the surface dust is a complex material, and what applies to pure

[*] 'Roy. Soc. Proc.,' A, vol. 90 (1914).

silica, etc., in the laboratory does not do so to the mixture, and probably the much larger scale of the experiment led to different results.

Specimens of road dust were collected from those places where observations had been made of the variations of the potential during the raising of dust clouds, either by the wind, or more generally by the passing of cars, and these were tested in the laboratory by the method already described,[*] which briefly is that a cloud of dust raised by a small bellows is projected against an insulated wire gauze screen connected to an electroscope, and the charge upon the latter tested   The air accompanying the dust is carried on, and its charge indicated by a radium collector attached to another electroscope. The charges thus obtained were found to be opposite in sign   The charge upon the air is the most satisfactory one to deal with, as it persists for a long time   Testing in this way it was found that all specimens of dust gave rise to a charge upon the air, the magnitude of the charge varying with the degree of fineness, and also with its nature, whilst the sign of the charge depended upon the chemical composition   Merely shaking a duster is quite sufficient to produce an easily measurable change, so that a very small amount of material is quite sufficient to produce a measurable charge in a room.

The curve (fig 2) shows how the presence of dust disturbs the normal gradient   The normal curve was obtained at some distance away from the
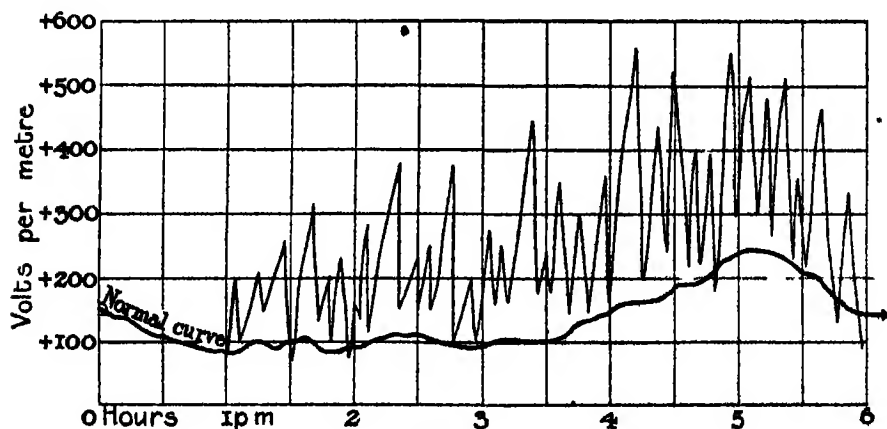
Fig. 2.

town, the other was taken on Hills Road, Cambridge.   Here every passing vehicle which raises dust makes its presence felt   Only a few of the points of change of potential are shown on the diagram, for even the passage of a

[*] 'Roy. Soc. Proc.,' A, vol 90 (1914).

bicycle along a dusty road produces some disturbance   The curve is a little diagrammatic, as it is the result of eye observations, but it well represents the extraordinary fluctuations due to the dust.

Many hundreds of observations have been taken in England and on the Continent, in addition to those mentioned in Africa, and some of these, which are typical of the rest, are given in Table I, which refers to road dusts obtained from Glamorgan

Through the kindness of the County Surveyor, Mr. G. A Phillips, I have been able to make an interesting set of observations on the dust from various roads in his district   The materials used are of many kinds, and of known origin   They may roughly be divided into siliceous and calcareous, and the electrification obtained with the clean dust was generally of the sign which might have been predicted from the nature of the material   The material from the roads varied very much in the degree of fineness, and also in the amount of organic matter present.   Some of the siliceous specimens contained calcium carbonate in measurable amount   The limestones naturally were nearly all calcium carbonate, but the other samples probably contained the carbonate as an accidental contamination   In several instances given in the Table it is seen that granitic and basaltic dusts give positive charges to the air instead of negative, as would have been anticipated from the nature of the material, but this was due to the dust really being composed of a mixture, as the following experiments show.

A portion of the basaltic dust from the Ely and Cowbridge road was treated with excess of HCl, and the insoluble residue washed and dried   This residue on spraying in the usual manner gave a — charge to air and + to gauze, showing
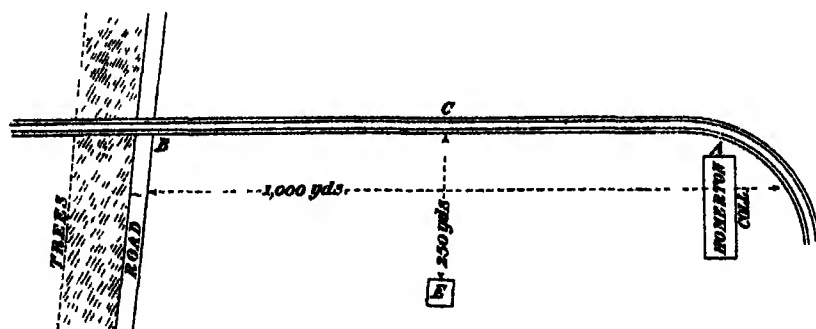
Fig. 3.

that the opposite effect obtained with the untreated dust was due to the presence of calcium carbonate.   A similar result was obtained with granite dust containing organic matter after the latter had been burnt off, so that it

may be reasonably inferred that a purely siliceous dust would always give rise to a negative charge in the air

Table I

Origin of material	Nature and appearance	Charge given to air by wind, etc	Laboratory test	
			Charge on air	Charge on gauze
Olchfa Bridge	Granite Grey coarse dust, with little organic matter	—	—	+
Mafan Road	Limestone White fine powder, with little organic matter	+	+ Weak	— Very weak
Neath Road	Limestone Light grey fine dust	+	+ Weak	— Weak
Cowbridge Road	Basalt Coarse dust, with little organic matter	—	— Strong	+ Fair
Redhall and Nottage Road	Limestone Very fine dust, with much organic matter	+	+ Strong	— Fair
—— Road	Basalt Grey coarse powder	—	— Very strong	+ Strong
Neath to Pontwhally Road	Granite Light-grey fine dust	—	— Very strong	+ Very strong
Gwangleda Bridge	Limestone Pink fine dust, with some organic matter	+	+ Fair	— Weak and uncertain
Boat and Nantgeon Road	Granite Dark fine dust, with much organic matter	+	— Fair	+ Fair .
Neath and Port Talbot Road	Granite Very fine dust, with lot of carbonate	+	— Very weak	0
Beaufort and Pontardulais Road	Limestone Fine grey dust	+	+ After some time	— Weak
Port Talbot Road	Limestone Fine dust, with little organic matter	+	+ Very strong	— Fair
Maesgwyn .	Granite Coarse grey, no organic matter	—	— Very strong	+ Strong
Pontypridd . .	Basalt Dark grey coarse powder, small organic matter	—	— Very strong	+ Very strong
Penwyll Road .	Limestone Fine dust	+	+ Strong	— Weak
"Coopers' Arms"	Basalt Dark grey coarse dust	—	— Fair	+ Strong
Road, fourth mile from Cardiff	Basalt. Dark grey powder, with carbonate and organic matter	+	— Fair	+ Fair

Table II—*continued.*

Origin of material	Nature and appearance	Charge given to air by wind, etc	Laboratory test	
			Charge on air	Charge on gauze
Llandaff Road	Limestone Very fine dust	+	+ Fair	— Weak
Ely and Cowbridge Road, fifth mile from Cardiff	Basalt Grey coarse dust, with organic matter	+	— Weak	+ Very weak
Ely and Cowbridge Road, ninth mile from Cardiff	Limestone Grey dust, with much organic matter	+	+	— Weak
Near Pyll Station	Limestone Fine light dust	+	+ Very strong	— Fair

2   *Manufacturing Operations, etc*

Several Portland cement works are situated near Cambridge and these have a very marked influence upon the potential gradient in their neighbourhood The gradient is enormously increased by the action of two factors   (1) steam escaping from the engine, (2) the cloud of cement dust which envelops the works   Both steam and cement dust give to the atmosphere a positive charge and it does not seem possible to determine the amount due to each cause, but the local effect of the two together is very great

The " Norman " Cement Works are about 1½ miles from the town and can be approached in one or two directions almost free from trees   A calm day after rain is a satisfactory one for making a set of determinations   Using a Wulf electrometer, readings were taken at different distances from the works until the potential indicated was the same as the average previously found for the neighbourhood   The distance was measured by pacing, and the electrometer had to be supported at different distances above the ground in order to meet the varying potential gradient   This was really very unsatisfactory, as the observer's body exerted a considerable influence, but a better arrangement could not readily be devised because the whole series of observations must be taken during a short interval of time when the normal potential gradient is steady.   Table II gives the record of the results obtained on February 12, 1913.

Measurements were taken both going to and returning from the works, the whole time taken being about an hour.   A rapid tour round Cambridge in a motor car just before and after the determination gave the average value for the potential gradient as about 75 volts per metre.   At other cement works in the neighbourhood the same effect was seen, and at Pretoria the same

Table II

Distance from works	Potential gradient
paces.	volts per metre
100	580
150	540
200	420
300	360
400	300
500	250
600	210
700	180
800	130
900	90
1000	75
1100	70
1200	70

thing had been previously observed   Portland cement is a mixture of many things, but is composed mainly of silicates, and the increase of the positive potential produced by its agency is thus the same as that derived from the mixture of materials composing road dust   Inside the factory itself the gradient was so high that it could not be found with the electrometer used.

The author has shown[*] the great influence of the fine siliceous dust blown from the mine refuse heaps in the neighbourhood of Johannesburg. This refuse consists almost entirely of very finely divided quartz, and when a wind is blowing large clouds of it are raised, with the result that the positive potential is completely reversed and a negative value given, which can be detected for a distance of nearly a mile away from the mines in the direction in which the wind is blowing, but for a much shorter distance in the other direction

The unloading of coal from a truck in a railway yard, or even the emptying of sacks in the cellar, gives rise to a positive charge upon the air. Some recent observations taken in coal mines show that considerable charges arise during the hewing of the coal if any quantity of dust is produced. The same thing is seen inside a flour mill, and no doubt every industry which results in the formation of a cloud of dust gives rise to some change in the atmospheric charge   Even ordinary domestic operations, such as sweeping a carpet or shaking a duster, produce a local influence   The air of a room after sweeping is usually charged positively.   Shaking a tree, the blossoms of which are laden with pollen, produces an increase of the positive charge.   This was very noticeable in the case of the bog myrtle and also

* 'Trans. Roy Soc. South Africa,' vol. 2 (1912).

with the yew. Kahler[*] has noted the same thing from the pine trees in the neighbourhood of Potsdam.

3 *Influence of Steam*

Since the time when Armstrong devised his hydro-electric machine, it has been generally known that the escape of steam under pressure was accompanied by strong electrification, but as far as I know no one—with the exception of Lord Kelvin, with whose work[†] I have recently become acquainted—has called attention to the great increase in the normal atmospheric potential gradient produced by steam escaping from ordinary engines

The author's attention was first called to the influence of steam when taking observations on the potential gradient at the top of Van Reenan's Pass, between the Orange Free State and Natal. It was then noted that after a train had passed a few hundred feet away a considerable rise in the positive potential occurred, and this increase persisted for some time after the disappearance of the steam Further observations taken at many places, even in the heart of the City of London, have confirmed this The change in the potential was determined in the usual way with an electroscope furnished with a radium collector

Recently some work has been done at Cambridge on the influence exerted by the clouds of steam emitted by locomotive engines, the details of which are given below. The country round Cambridge is flat, and many spots may be chosen near to the railway where there are few trees to screen the effects and sufficiently far from roads to be out of the range of the dust influence Observations were taken at stations at different distances from the line, and the magnitude of the potential gradient noted after the passage of a train under steam The mere passing of a train had no influence, unless as sometimes happened in very dry weather a lot of dust was raised , for the potential to be largely increased it was necessary for steam to be escaping either in the usual way from the funnel, or even by blowing off from the safety valve. As already noted the charge persisted after the cloud of steam had disappeared, so that if the distance of the observing station from the line was sufficient, a train might be out of sight before the change in the potential would be recorded. A convenient station was situated in a field off the Hills Road just outside Cambridge.

The observations were made with a Wulf electrometer furnished with a radium collector, and records were made of the potential indicated by that

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[*] 'Phys Zeit,' vol 13, p. 1216.
[†] 'Papers on Electrostatics and Magnetism,' § 397.

instrument at definite intervals of time   The plan given in fig. 4 shows the
relative position of the railway and the observing station   The trains from
Cambridge became visible at A and passed out of sight at B, and Table IV
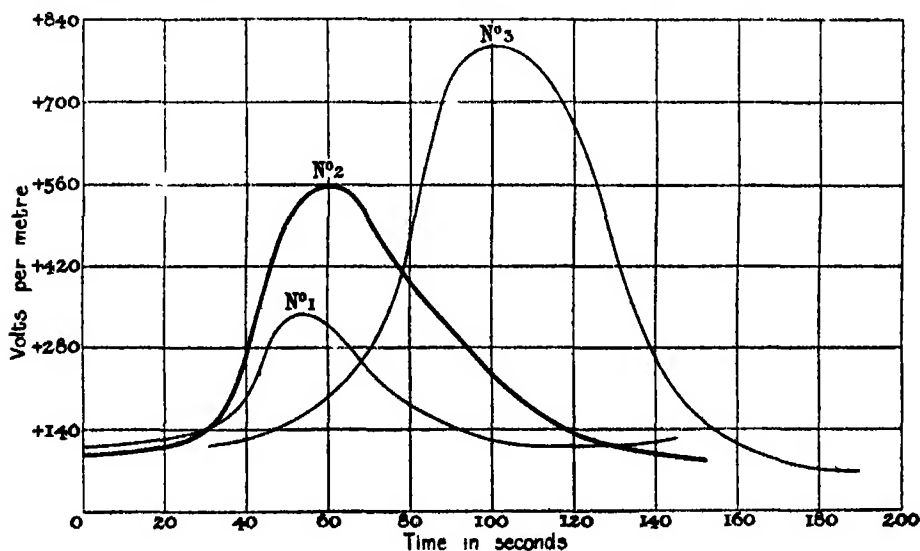
Fig 4

shows that the influence of the steam was not manifested until the train had
passed beyond the latter point   The position E was about 250 yards from
the line

The recording was continued until the potential had fallen to its initial
value, or until the passing of a second train produced another disturbance.

The effect was thus noticeable for about six minutes after the passing of
the trains.

Table III gives a typical record   The potentials are given in terms of the
scale reading of the electrometer, and, when the threads were beyond the
field of view, the gradient must have been over 700 volts per metre   The
normal value of the gradient was about 120 volts per metre. The curves
(fig 4) show how the magnitude of the potential varies with the class of
train, the one giving the greatest volume of steam produces the greatest
change in the potential   Curve No 1 is a slow "stopping" train, No. 2 a
goods train, and No 3 a heavy "express."   The last curve is displaced
25 seconds to the right for clearness   The time elapsing before the change
in the potential due to the steam reached the recording instrument depended
to some extent upon the direction and strength of the wind.   In practically
calm weather the disturbance extended uniformly a considerable distance
from the place where the steam was emitted, but it was carried a greater

Table III.—July 12, Hills Road Station. Wind S W   Train to London.
Heavy Express.

Time	Reading	
sec		
0	18	Train at A
15	18	„ C
30	19	„ B
45	20	
60	18	
90	20	
120	25	
130	30	
135	60	
140	80	
200	—	} Too great to be measured by electrometer
230	—	
260	80	
270	70	
280	62	
300	50	
310	35	
315	30	
330	24	
360	22	
400	21	

distance with the wind   Some records were taken simultaneously on both sides of the line when the wind was blowing from south-west at an angle across it   The electrometers were placed about 150 yards from the line Table IV gives the results, and the effect of wind is very distinctly shown

Table IV —Heavy Express Train

North station		South station	
Time	Deflection	Time	Deflection
sec	divisions	sec	divisions
0	19	0	20
15	21	15	22
30	35	30	22
45	65	45	20
60	80	60	36
75	—	75	45
90	—	90	56
105	80	105	30
120	62	120	24
135	38	135	20
150	25	150	20
165	22	165	20
180	20	180	20

The distance from the line to which the influence of the steam extends may, in certain cases with the wind, reach a distance of nearly a mile, and the time taken before the electrometer indicates any change may be from four to five minutes

The curve (fig 5) gives the results obtained at a distance of nearly 1000 yards, the potential changing from 70 volts per metre to about 200
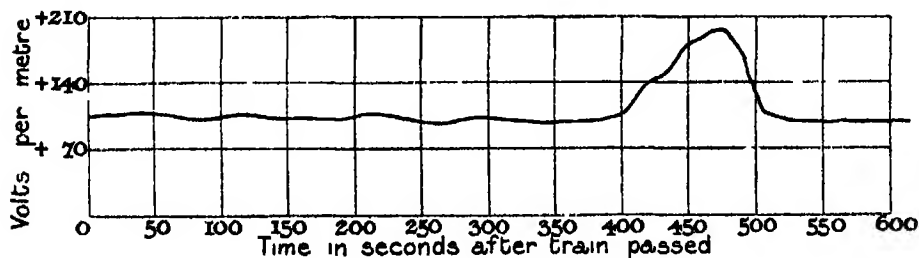
Fig 5

The influence of steam may be detected on a moving train   When a cloud of steam is trailing behind, an electroscope, furnished with a radium collector, will indicate a strong charge even inside the carriage, if the window is open   Inside a tunnel a very strong charge can be detected, sufficient to send the gold leaf out at right angles to its support   Inside a boiler-house the same thing is seen if the steam is escaping under pressure, and here, too, the charge persists in the air long after the cloud has disappeared.

My acknowledgments are due to Prof Sir J J Thomson for the use of the Cavendish Laboratory, where a portion of the work was carried out.

Summary

1 From these observations, the conclusion may be drawn that sudden variations of the atmospheric potential gradient may be due to local circumstances.

2 The presence of dust in the atmosphere has the effect of altering the potential gradient, sometimes increasing sometimes diminishing the positive value.   The dust from well used old roads practically always increases the ' positive potential

3 Manufacturing operations which result in the production of dust disturb locally the potential gradient.

4 The presence of clouds of steam increases the positive potential, and the effect persists for some time after the steam has condensed.

The 27-Day Period in Magnetic Phenomena.

By C. CHREE, Sc.D., LL.D., F.R.S.

§ 1. In two earlier papers, termed here for brevity SM₁* and SM₂,† I have discussed data supporting the existence of a period of about 27 days in. magnetic phenomena. The results have, I think, put it beyond question that there has been—at all events since 1890—a decided tendency for the magnetic character of a day, whether disturbed or quiet, to resemble that of a day either 27 days earlier or 27 days later more closely than it does that of the average day. There is no period—or, if there is, its amplitude is very small—in the usual sense of the word, the phenomena do not go on repeating themselves in an indefinite sequence like the phenomena of day and night. Various ways suggest themselves of prosecuting the enquiry further, with a view to ascertaining its connection with other natural occurrences, especially with sunspots or other solar phenomena. Having at hand a long series of magnetic records, the method that appeals to me as a practical man is the utilisation of these records. The next question is how to use them to best advantage.

If the 27-day period, as we may term it for brevity, is directly associated with sunspots, we should expect it to be influenced by the difference between the solar latitude of sunspots in years of many and few sunspots. My previous work has shown that the period, though ordinarily far from insignificant, may sometimes be little in evidence. There is much that in the present state of our knowledge must be regarded as "accidental" in magnetic phenomena, and a few "accidents" conspiring together may render the 27-day period unapparent in an individual year. Thus, for an enquiry into the nature of the relationship, if any, between the period and sunspots, or any other solar or lunar phenomenon, data are wanted from a period so long that accidental phenomena will be largely eliminated from the groups of years representative of any one given set of conditions such as sunspot maximum or minimum. As a preliminary to any such general enquiry, the measure of magnetic disturbance to be adopted claims consideration. The measure adopted in SM₂, and also mainly in SM₁, was the "character" of the day on the international scale 0 (quiet), 1 (moderately disturbed), 2 (highly disturbed). Since 1906 mean "character" figures taken out to 0·1, based on

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the data from a large number of stations, have been published at De Bilt These enable the days of each month to be arranged easily, and probably with adequate accuracy, in the order of their disturbance It is, however, impossible to say how the day whose character in the international lists is, say, 0 5 compares with the day whose international figure is, say, 1 5 If one takes the "activity" of the day as defined by Prof Bidlingmaier, which represents practically the integral of the squares of instantaneous departures from a normal value, the day whose international figure is 1 8 is much more than twice as disturbed as the day whose international figure is 0 9. There is a good deal to be said for "activity" as a measure of disturbance, but activity data are practically non-existent, and deriving them for any considerable period of years would represent an enormous deal of labour. A second objection is that there are a few days whose "activity" is so enormously greater than that of the average day that an "accidental" occurrence of two of these might introduce a false period into the records of even a number of years

International "character" figures, if available for years prior to 1906, would have much to recommend them Their unprejudiced nature is above suspicion, and their aid enables one to separate out at once the five most and the five least disturbed days of the month, five being a number which is generally recognised as at least convenient But international data do not exist prior to 1906, so one must use something else. In SM₁, in the main, I took as a measure of disturbance "character" figures 0, 1, 2, which I allotted myself from consideration of the Kew curves alone One can allot "character" figures on this scheme to the days of a whole year in a couple of days or less, and the summation of columns containing only 0's, 1's, and 2's is simplicity itself Naturally, however, one has more than five 0's and fewer than five 2's a month Thus characterisation from a single station does not lend itself to the selection of a fixed number of days of a particular class.

In SM₁, dealing with the years 1890–1900, I considered only the five most disturbed days of the month, and took the amplitude of the horizontal force range as the criterion of disturbance in their selection. Treated in this way the years 1890–1900, as a whole, showed the 27-day period as unmistakably as did the years 1906–1911 dealt with in SM₃. I felt, however, at the time that the hybrid nature of the method—i e the selection of the days by reference to the horizontal force range, but the measurement of the disturbance by reference to the "character" figure—might arouse criticism, and partly for that reason, partly for my own satisfaction, I considered for two years, 1894 and 1895, the result of taking the range of H as itself the measure of the disturbance I found that in 1895 the 27-day period was

"as unmistakable in the range as in the character figures," but "in 1894 the character figures and the range figures both show not a peak at day $n+27$ or $n+28$ (n being the representative selected disturbed day), but a high plateau from about day $n+25$ to day $n+34$ The range figures, in fact, would seem to favour a Schmidt or 30-day period."* The substitution of range figures for "character" figures added largely to the arithmetical labour, and I did not prosecute the enquiry further   It seemed, however, desirable to undertake this labour now, to see whether the method was likely to prove a satisfactory one for dealing with years prior to 1890

§ 2 Daily ranges at Kew for D (declination), H (horizontal force), and V (vertical force) being now at my disposal, it seemed desirable to obtain results from all three elements, so as to compare their relative advantages for the object in view   The five days of largest daily range were taken as the five most disturbed days, the D, H, or V range serving as the criterion of selection according to the element which was being used as the measure of magnetic disturbance   The five days a month which the Astronomer Royal had selected as representative quiet days were accepted as the five quietest days   The latter choice, I dare say, might be improved on for purposes such as the present   The desirability of securing that the mean time represented by the selected quiet days should fall near the middle of the month exerted, I believe, some influence on the Greenwich choice   In a good many cases the selected days are obviously not the quietest of the month, and if one cared to spend a lot of time, a choice somewhat superior for the present purpose could doubtless be made   But the Astronomer Royal's days have at least the great advantage of being free from any suspicion of bias   A choice of quiet days based on the diurnal range alone has several disadvantages   The differences amongst the ranges of the 10 or 15 quietest days of the month are usually not large   In many cases there would be several ties amongst the days competing for the choice, and the difference in range between days selected and days not selected would frequently be of the same order as the probable error of measurement   This is especially true of H and V, where temperature corrections are usually necessary to the measured curve ordinates   No continuous record of temperature in the magnetograph room had been obtained at Kew until 1894   Temperature corrections to the ranges were thus impossible for the earlier years, and under these circumstances it appeared best to omit such corrections entirely. The uncertainty arising from the absence of a temperature correction to Kew H ranges is trifling, but this is unfortunately by no means true of V   A choice of the five quietest days of the month based on

* *Loc. cit.,* p. 104.

the ranges, especially V ranges, would be an uncertain one, especially at seasons when the magnetograph room temperature is altering most rapidly. The absence of a temperature correction is seldom serious in the choice of the five most disturbed days of the month, because the ranges on the most disturbed days usually stand conspicuous above the others. Still the fact remains that a few even of the Astronomer Royal's quiet days figured amongst the five days of largest V range, and their inclusion was more likely due to large temperature range than to real disturbance. It is only proper to mention this, but it should at the same time be pointed out that irregular variations are very rare in V as compared with H or D curves, and a quiet day has often a large regular diurnal variation.

§ 3 Owing to the necessity of reducing arithmetical computation to a minimum, attention was confined to the ranges on days $n-2$, $n-1$, n, $n+1$, $n+2$, and $n+25$ to $n+30$ inclusive, n being a representative selected day, disturbed or quiet. The five days $n-2$ to $n+2$ served to show the nature of the preliminary "pulse"—whether representing excess above the normal on disturbed days or deficiency on quiet days—while the six days $n+25$ to $n+30$ represented the secondary pulse constituting the 27-day period. No days were selected for December, 1900, as the corresponding secondary pulse would have fallen in 1901. This left 131 months, and so 655 selected days of either type, or 1310 in all. Consequently, the total entries of daily ranges in the 11 columns numbered 14,410 for each element. The D ranges were measured directly in minutes of arc to 0 1', but the H and V ranges in millimetres, going in each case to 0 1 mm. In the majority of cases, in the H and V curves, 1 mm represented 5 γ throughout the entire year, but in some cases changes of the order of 2 per cent. or more occurred in the course of 12 months. For the purposes of the present enquiry, it was unnecessary to take account of small variations, incapable of affecting sensibly the relative values of the means derived from the successive columns of figures, thus the readings taken in millimetres were usually not converted individually into force, but were treated as if the equivalent of 1 mm. were always the same. In the first instance, each year was considered separately, and the selected disturbed and quiet days independently. The sum of the ranges from the 60 selected days (55 in 1900) appearing in each column was formed, and expressed as a percentage of the mean range from all days of the year multiplied by 60 (in 1900 by 55). Tables I, II, and III give the percentage figures thus obtained for D, H, and V separately. Table IV shows the arithmetic mean of the D, H, and V percentages. The percentages were all calculated to 0·1, but the last figure has been omitted, except in the final means.

Table I.—D Ranges. Percentage of Mean Absolute Daily Range

Year	Five days of largest D range and associated days										
	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
1890	103	116	153	116	102	99	106	106	104	107	111
1891	105	124	172	127	115	102	115	114	123	115	106
1892	91	136	196	129	104	93	93	108	108	103	98
1893	99	116	155	118	104	99	101	104	109	104	102
1894	94	123	193	132	108	92	100	100	108	107	116
1895	100	115	165	123	110	97	106	122	117	120	118
1896	103	127	180	141	118	108	116	121	122	116	99
1897	89	122	176	118	95	98	110	114	111	98	108
1898	102	138	187	129	103	105	106	121	122	122	106
1899	97	124	175	123	108	105	121	120	118	101	99
1900	99	115	155	106	99	97	102	96	95	93	103
Mean	98·3	123·2	178·5	123·9	105·9	99·5	106·9	111·4	111·6	107·9	105·6

Year	Five selected quiet days and associated days										
	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
1890	104	91	78	94	104	92	93	94	95	97	87
1891	94	82	73	95	100	99	80	92	90	104	113
1892	95	79	70	93	98	94	104	105	92	91	87
1893	93	86	76	92	100	91	91	95	105	102	102
1894	81	81	69	94	120	103	92	91	97	93	87
1895	100	91	68	90	108	96	90	89	105	102	106
1896	86	76	66	90	105	87	79	73	78	86	94
1897	91	84	67	90	94	90	78	95	94	107	101
1898	91	82	67	81	97	95	68	80	82	90	96
1899	84	80	69	88	108	87	87	90	91	97	105
1900	100	89	81	96	112	96	95	100	95	93	102
Mean	92·6	83·5	71·3	91·2	104·3	93·6	89·8	91·4	93·2	96·6	98·2

Table II.—H Ranges.   Percentage of Mean Absolute Daily Range.

Year	Five days of largest H range and associated days										
	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$.	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
1890	102	118	163	119	107	107	107	116	117	105	109
1891	104	128	181	130	114	95	104	104	111	107	110
1892	112	166	228	153	100	93	103	122	105	100	100
1893	96	123	170	128	103	101	101	116	114	110	104
1894	115	163	215	144	119	103	107	104	105	112	124
1895	110	133	171	124	109	109	116	129	120	115	105
1896	113	133	188	145	120	111	115	124	133	126	106
1897	97	122	172	125	103	96	105	117	109	101	102
1898	118	156	199	131	117	104	129	124	129	129	114
1899	118	133	180	129	118	105	119	132	126	113	103
1900	99	116	172	111	103	96	102	108	101	98	104
Mean	107·9	135·6	185·4	130·7	110·2	102·2	109·8	117·7	115·4	110·7	107·4

Year	Five selected quiet days and associated days										
	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+22$	$n+30$.
1890	99	88	74	92	105	96	89	87	89	102	94
1891	95	84	72	89	91	97	96	96	85	104	110
1892	92	74	61	86	85	94	90	104	90	89	85
1893	96	82	72	92	99	90	88	95	106	99	97
1894	76	75	64	92	119	102	93	89	95	91	82
1895	100	87	68	86	110	89	87	83	99	102	106
1896	87	73	62	85	96	83	83	73	77	88	96
1897	94	85	67	88	92	93	81	85	88	96	103
1898	89	71	60	73	102	96	67	75	78	88	98
1899	87	76	62	84	101	89	86	87	90	94	106
1900	95	83	79	97	111	97	92	100	94	97	108
Mean	91·9	79·8	67·2	87·9	100·8	93·2	85·4	86·5	90·3	95·1	98·5

Table III —V Ranges   Percentage of Mean Absolute Daily Range

Year	Five days of largest V range and associated days										
	n − 2	n − 1	n	n + 1	n + 2	n + 25	n + 26	n + 27	n + 28	n + 29	n + 30
1890	93	102	161	111	100	94	100	103	106	105	99
1891	111	147	210	143	118	98	112	121	126	107	111
1892	101	205	284	177	115	84	87	116	107	92	88
1893	99	124	202	129	100	94	101	118	111	102	102
1894	107	185	284	161	128	83	113	102	111	106	155
1895	112	132	191	129	99	105	115	140	130	108	108
1896	113	146	213	146	124	119	131	126	128	121	110
1897	90	121	192	121	97	96	111	104	107	107	102
1898	121	166	219	123	92	95	104	142	119	125	108
1899	112	140	185	139	113	103	119	116	109	99	90
1900	91	119	173	108	94	122	93	94	97	90	92
Mean	104 5	144·3	210 4	135 1	107 1	99 5	107 8	116·6	113·8	105 6	105 8

Year	Five selected quiet days and associated days										
	n − 2	n − 1	n	n + 1	n + 2	n + 25	n + 26	n + 27	n + 28	n + 29	n + 30
1890	99	91	90	92	108	99	99	89	95	98	97
1891	97	72	66	89	98	104	103	87	86	113	117
1892	86	70	56	79	90	91	88	113	89	85	82
1893	93	81	73	100	103	85	81	96	115	102	93
1894	64	61	51	106	133	108	83	88	97	90	73
1895	97	87	68	88	118	90	87	82	98	101	111
1896	87	75	65	85	99	91	88	79	80	85	89
1897	97	84	74	92	92	91	82	88	86	97	95
1898	81	77	68	77	107	98	85	73	75	83	106
1899	87	79	75	94	109	85	82	87	95	91	104
1900	93	86	90	93	112	95	93	105	102	99	102
Mean	89 1	78 3	70 5	90 4	106 3	94 2	88 3	89·9	92 4	94·9	97 2

Table IV —D, H and V Ranges   Means of Percentages from Tables I, II and III.

Year	Five days of largest range and associated days										
	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
1890	99	112	159	115	103	100	104	108	109	106	106
1891	107	133	167	133	115	99	110	113	120	110	109
1892	102	169	236	153	106	90	94	116	106	98	95
1893	99	121	176	125	102	98	101	113	111	105	103
1894	105	157	230	146	118	94	107	102	106	108	132
1895	107	127	176	125	106	104	112	130	122	115	109
1896	110	135	194	144	121	112	121	123	128	122	105
1897	92	122	180	122	98	97	109	112	109	102	104
1898	113	158	202	127	104	102	113	129	124	125	109
1899	109	132	180	130	113	104	120	123	116	104	97
1900	96	117	167	108	99	105	99	99	98	94	100
Mean	108 6	134 4	169 7	129 9	107 7	100 4	108 1	115 2	113 ·6	108 1	106 3
"Character" 1890–1900	110 9	150 ·0	216 ·5	158 9	123 ·9	101 5	118 5	134 8	132 0	120 9	113 7
1906–1911	101 5	144 4	201 1	154 ·6	116 7	98 4	112 8	126 5	121 6	112 5	106 ·2

Year	Five selected quiet days and associated days.										
	$n-2$	$n-1$	n	$n+1$	$n+2.$	$n+25$	$n+26$	$n+27.$	$n+28.$	$n+29.$	$n+30$
1890	100	90	81	93	106	95	94	90	98	99	93
1891	95	79	70	91	96	100	97	91	87	107	113
1892	91	74	62	86	91	93	94	107	90	89	85
1893	95	83	74	95	101	89	86	95	109	101	97
1894	74	72	61	97	124	104	90	89	96	92	81
1895	99	88	68	88	112	92	88	85	101	102	106
1896	87	74	64	87	100	67	83	75	78	86	93
1897	94	84	69	90	92	91	80	89	89	101	100
1898	87	77	65	77	102	96	87	76	78	65	100
1899	88	78	69	89	106	87	85	88	92	94	105
1900	96	86	83	96	112	96	93	102	97	96	104
Mean	91 2	80 5	69 7	89 8	103 8	93 ·7	88 9	89 9	92 0	95 ·5	96 ·0
"Character" 1890–1900	—	—	—	—	—	—	—	—	—	—	—
1906–1911	82 7	52 8	20 5	62 8	101 1	89 ·1	78 ·9	73 8	80 ·7	92 ·9	99 ·7

The last two lines in Table IV give, for purposes of comparison, corresponding percentages based respectively on the "character" figures assigned at Kew for the years 1890–1900 and the international character figures

calculated at De Bilt for the years 1906–1911   No quiet and associated day data existed for the earlier period

Considering first the range results from the years 1890–1900, it is seen that the general nature of the conclusions derived from the D, H, and V ranges is the same   All show the 27-day period distinctly, in the case alike of the disturbed and the quiet days   It is not quite clear what is a fair basis for comparing the three elements   On days $n+27$ and $n+28$, n being the representative day of largest range, the percentage figures are decidedly higher for V than for D, but the same is true of the representative days n themselves   If we take the excess over 100 in the percentage figure in column n as a measure of the primary pulse, and the corresponding excess in column $n+27$ or $n+28$—whichever is the larger—as a measure of the secondary pulse, the ratio of the secondary to the primary pulse has the values 0 158 for D, 0 207 for H, and 0 150 for V   The corresponding values of the ratios from the " character " figures were decidedly larger, being 0 299 for the years 1890-1900 and 0 262 for the years 1906-1911

§ 4   In Table IV, 1900 is the only year in which the percentages for days 27 and 28 subsequent to the representative disturbed day fall below 100   This year was very quiet, and the difference between the average selected disturbed and the normal day unusually small   Also a marked decline took place in disturbance throughout the year   Thus the range of the second of two days separated by 27 days tended to be slightly the smaller, irrespective of whether the first was a selected disturbed day or not   In Table IV, except in 1900 and 1894, the largest percentage in the days included in the secondary pulse following the selected disturbed days occurs either in column $n+27$ or column $n+28$ But in 1894 much the largest percentage appears in column $n+30$ This is true of all the elements, especially V, the average range for that element on day $n+30$ being actually 55 per cent above that of the normal day   That the average range from 60 days selected on a principle which takes account only of what happened 30 days earlier should exceed the normal by 55 per cent appears, at least at first sight, a phenomenon impossible to attribute to chance.   It seemed desirable to look into this more closely, as it suggested that in 1894—a highly disturbed year—the period of 30 days which Prof Ad. Schmidt has observed in specially large storms was abnormally developed   The first question was whether the specially large disturbances of V followed one another at 30 days' interval

In the whole 11 years there were only 18 days on which the V range exceeded 300 γ, and 8 of these occurred in 1894   Entering the ranges from these eight days in the order of their magnitude in the column headed n,

and distinguishing by heavy type ranges from selected disturbed days, the facts are as presented in Table V

Table V.—Apparent 30-day Period in 1894.　V Ranges (Unit 1 γ)

$n-31$	$n-30$	n	$n+30$	$n+31$
67	25	688	41	508
638	229	508	132	124
16	51	429	40	26
34	19	410	26	27
226	82	362	52	31
52	48	306	29	57
59	52	304	51	29
34	226	302	45	52

The largest range of all, 638 γ, was followed 31 days later by the second largest range, 508 γ, but this was the only case in which two of these specially large disturbances showed a 30- or 31-day sequence The phenomenon does not seem to be explained by Schmidt's period, but to be due to the "accident" that the day 30 days earlier than a day of specially large V range was in six cases out of eight a selected disturbed day. In four of these six cases, the first disturbance was quite trifling Even in 1894 the normal V range was only 46 γ, so that the incidence in column $n+30$ of Table III of the six days specified above, having an aggregate range of 2211 γ, produced an enormous effect It may be added that column $n+27$ of Table III included only one of the above eight days of largest V range.

The fact that the lowest percentage in 1894 in the secondary pulse associated with the selected quiet days occurs in column $n+30$ of Table III is also remarkable

Another outstanding result is the occurrence, in 1892, of 113 and 107 in column $n+27$ of Tables III and IV respectively, n being in this case the representative quiet day

In 1892 there were 28 occasions when the V range exceeded 100 γ, and of these no less than 9 occurred 27 days after one of the Astronomer Royal's quiet days If the data under review had been confined to 1892 and 1894—the two most disturbed of the 11 years—it is difficult to say what conclusions might not have been drawn Without investigating the records from similarly disturbed earlier years, we do not know what significance to attach to this

§ 5 It has been already remarked that a gradual decline in disturbance, such as distinguished 1900, naturally reduces the amplitude of the secondary

pulse of disturbance. An analogous effect follows from the ordinary seasonal change in the daily range If we express all ranges in terms of the mean daily range from the whole year, the consequence is to reduce the apparent amplitude of the secondary disturbance pulse in the beginning of winter, when the daily range is falling, and to correspondingly enhance it in the end of winter, when the range is rising This defect could be reduced, though not wholly removed, by expressing all ranges as percentages of the normal range for the particular month in which they occur This may be necessary for an exhaustive enquiry as to how the 27-day period varies throughout the year It would entail, of course, much extra labour The same object may, however, be attained fairly satisfactorily in a simpler way, by taking the difference between the pulses associated respectively with disturbed and with quiet days Any common tendency, whether to enhanced or diminished daily range, is then largely eliminated Table VI gives percentage differences obtained in this way for the several ranges and "character" figures It is confined in each case to the whole period dealt with, but corresponding results for the ranges in individual years can be deduced from Tables I–IV

Table VI.—Excess of Percentages from 5 Highly Disturbed and Associated Days over Percentages from 5 Selected Quiet and Associated Days

	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
1890–1900—											
D ranges	5 7	39 7	102 2	32 7	1 6	5 9	17 1	20 0	18 4	11 3	7 4
H „	16 0	55 8	118 2	42 8	9 4	9 0	21 4	29 2	25 1	15 6	8 9
V „	15 4	66 0	139 9	44 7	0 8	5 8	19 5	26 7	21 4	10 7	8 6
Mean D, H, and V ranges	12 4	53 9	120 0	40 1	3 9	6 7	19 2	25 3	21 6	12 6	8 3
1906–1911—											
International "character"	18 8	91 6	180 6	92 3	15 6	9 3	38 9	53 2	40 9	19 6	6 5

In Table VI the figure in column $n+27$ is always substantially greater than that in column $n+28$, and the figure in column $n+28$ always exceeds that in column $n+26$. This suggests, of course, as dominant a period in excess of 27 days, but considerably nearer 27 days than 28. The data, however, in Tables I–IV for the days associated with the selected quiet days suggest a period somewhat nearer 26 than 27 days, while the 11-year mean data from days associated with disturbed days in Table I suggest a period slightly in excess of $27\frac{1}{2}$ days. This is distinctly suggestive of a possibility, pointed to by some results in SM_2, that the period tends to lengthen as the standard of disturbance represented in the primary pulse is increased

§ 6. If five days were selected by lot from each month, the expectation that

the 27th day before (or after) one of these days would be itself a selected day would be roughly 60/365, *i.e* the event would happen in about 16½ per cent of the days   Taking the 655 selected days of one type from 10 years 11 months, one would thus expect such a sequence on about 108 occasions Table VII shows how often selected days of specified types showed a 27-day sequence

Table VII —27-Day Sequences of Selected Days

First day	Disturbed				Quiet	Quiet	Disturbed
Second day	Disturbed				Quiet	Disturbed.	Quiet.
Element	D	H	V	D, H, and V, mean	—	H	H
Year							
1890	10	16	12	13	12	3	9
1891	15	13	16	15	14	7	7
1892	11	12	12	12	11	12	7
1893	11	20	15	15	15	10	6
1894	14	16	13	14	13	4	10
1895	16	19	22	19	14	3	7
1896	25	22	22	23	21	3	8
1897	16	14	14	15	13	2	4
1898	19	19	20	19	17	1	8
1899	15	19	16	17	14	5	7
1900	12	16	7	12	9	7	9
Total	164	186	169	173	153	57	72

The sequence of a disturbed day by a disturbed day, it will be seen, was *decidedly more frequent* for H than for D or V   Also, whichever of the three elements one takes, the sequence of a disturbed day by a disturbed day was more frequent than the sequence of a quiet day by a quiet day   This is what we should expect on any hypothesis, because the selected disturbed days were more outstanding as representatives of disturbance than were the Astronomer Royal's days as representatives of quiet conditions   Even for the quiet days the sequences were more numerous by 40 per cent. than they would have been according to pure chance ; 1896 showed an outstandingly large number of sequences, whether of disturbed days by disturbed days, or quiet days by quiet days.

The cases in which a selected quiet day was followed by a selected disturbed·day were, on the whole, decidedly fewer than those in which the converse phenomenon occurred.   The remarkable prevalence, however, of the former phenomenon in 1892 has been already remarked on.

The number of 28-day sequences of disturbed days was also investigated for the H ranges   Taking the years in chronological order the numbers were respectively 17, 12, 8, 11, 16, 16, 20, 11, 22, 14, 15

The total 162 is less by 24 than for the corresponding 27-day sequence 1898 showed the largest number of 28-day sequences, and 1892 the fewest.

§ 7   Taking the H disturbances, it was investigated how far sequences of 27 days could be traced   The results were as follows —

Sequence of 27 days {	2 days or more	3 days or more	4 days or more	5 days or more	6 days or more	7 days or more	8 days
Number of cases	186	32	17	7	2	1	1

The 32 cases are included in the 186, the 17 in the 32, and so on   Thus in the 32 cases where there were three or more sequences the second of the two days was at once the second day of one sequence of two, and the first day of another sequence of two   The longest sequence, covering 7×27 or 189 days, began on December 10, 1895, and ended on June 16, 1896   The next longest extended from December 20, 1897, to May 4, 1898

Several things have to be borne in mind when dealing with apparent sequences   If a disturbance were a sharply marked incident of short duration and if its recurrence period, if it recurred at all, were $27 + f$ days, where f is a definite fraction of 24 hours, then the number of apparent recurrences obtained as above could not exceed $r \equiv (24 - N)/f$, where N is the hour of the first occurrence   There might be more than r recurrences, but the $(r+1)$th would fall on the 28th day not the 27th after the rth.   The number of apparent 27-day recurrences could not exceed $24/f$, and a limit might thus be found for f.   For instance, if we accepted 7 as the maximum possible number of recurrences, the limiting value of f would be $3\frac{3}{7}$ hours.   A disturbance, however, is not a shaply marked incident, and disturbed conditions are often shared by two or more consecutive days.

Also the chances against an apparent sequence being a real one would seem to be not inconsiderable, in view of the fact that about 9 per cent. even of the Astronomer Royal's quiet days had for the 27th day thereafter a selected disturbed day   This, of course, tends to emphasize the desirability of finding some criterion for discriminating between true and apparent sequences.

§ 8. The first thing one naturally looks to when in quest of a criterion is the relative size of disturbances forming an apparent sequence.   A sunspot, for instance, often develops very rapidly, but is seldom large for more than one

solar revolution   An investigation was thus made into the amplitudes of the 186 H ranges which showed a 27-day sequence.

Table VIII shows the average size of the ranges on the first and second occurrences, and for comparison the average size of the range from all the selected disturbed days of the year   It also gives the number of times when the first range of the sequence exceeded the second or fell short of it.   It should be remembered that the 186 cases included 32 in which the sequence extended to three or more days, and in these cases at least the second member of the sequence figured as the second day of one sequence and the first of another The ranges are given as measured in millimetres.   The value of 1 mm was usually 5 0 γ, but in some years it departed from this by 1 or 2 per cent

<div align="center">Table VIII —H Ranges forming Sequences of Two</div>

Year	Ranges in mm (1 mm = 5 γ approx)			Number of occasions when	
	Average disturbed day	First day of sequence	Second day of sequence	First range the larger	Second range the larger
1890	14 ·5	16 ·5	16 4	9	7
1891	22 ·0	18 4	18 4	7	6
1892	38 3	47 ·0	47 3	7	5
1893	23 4	22 9	22 9	9	10
1894	34 3	29 5	25 ·9	10	6
1895	22 8	25 7	24 1	10	9
1896	23 ·8	24 1	22 9	12	10
1897	17 5	18 5	18 7	8	6
1898	21 9	21 8	21 5	10	9
1899	17 5	18 7	17 7	9	9
1900	13 2	14 ·6	12 ·9	8	8
Totals or means }	22 ·7	23 4	22 6	99	85

On two occasions, the first in 1893, the second in 1898, the ranges were equal.

It will be seen that in most individual years the range on the first day of a sequence was more often than not the larger, and on the average from the 11 years the first day's range was some 4 per cent. in excess of the second day's.   But in 1890, 1891, 1892, 1893, 1897, and 1898 the difference between the mean ranges from the first and second days of a sequence was almost microscopic

§ 9 The cases of three or more sequences led to the results given in Table IX.   The ranges in this case are given in millimetres, and in forming the means the value of 1 mm. was treated as invariable, which was not always strictly the case.

Table IX.—H Ranges (in mm) in Days forming Sequences of Disturbances.

	First day	Second day	Third day	Fourth day	Fifth day	Sixth day	Seventh day	Eighth day
32 sequences of 3 days	22 1	20 5	24 1					
31 ,, 3 ,,	22 3	20 5	20 3					
17 ,, 4 ,,	22 9	21 6	27 7	22 0				
16 ,, 4 ,,	23 4	21 6	20 5	19 7				
7 ,, 5 ,,	25 2	22 4	21 0	22 5	21 9			
6 ,, 5 ,,	18 9	21 5	20 2	22 5	20 7			
1 ,, 6 ,,	30 9	17 ·0	19 1	23 9	20 9	22 3		
1 ,, 8 ,,	16 1	21 1	27 6	22 2	25 ·0	17 4	26 6	22 2

Two sets of results are given for the sequences of three, four, and five days, because the means derived from the full number of cases, whether 32, 17, or 7, were largely influenced by one outstanding day. February 13, 1892, the most disturbed day of the whole 11 years, figured as the third day of a sequence of four, the ranges of which in millimetres ran as follows .—

$$15\,4 \qquad 20\,7 \qquad 144\,0 \qquad 59\,5$$

The run of the ranges suggests that the connection of the 144 mm range with those preceding it may well have been accidental, and in any case the omission of this outstanding occasion from the three- and four-day sequences seemed likely to lead to a more representative result than its inclusion Omitting this day, there does seem a tendency to reduction in the range of the later members of the three- and four-day sequences, but it is very slight.

The five-day sequence omitted in forming the third last line of Table IX began with a range of 63 3 mm, which was much the largest found on the first day of any of the sequences, the next in size being only 42 9 mm. These two ranges occurred on successive days, forming two of a remarkable succession of highly disturbed days, February 21–25, 1894 The ranges in millimetres on these five days and on successive groups of five days separated by 27-day intervals were as follows :—

						Monthly mean.
February 21 to 25	85 ·7	30 ·6	63 3	42 9	67 7	19 ·3
March 20 ,, 24	11 1	14 5	27 ·7	25 0	13 4	15 4
April 16 ,, 20	11 ·0	22 ·6	26 ·2	20 ·4	15 ·5	15 5
May 13 ,, 17	17 ·0	22 8	22 ·2	20 9	14 ·2	16 ·2
June 9 ,, 13	27 ·8	45 ·1	22 ·2	16 ·9	16 ·6	18 6
July 6 ,, 10	14 ·0	13 ·2	17 ·6	20 ·8	13 4	20 ·9

The mean range from all days of each month is shown for comparison Heavy type indicates a day which qualified as a disturbed day. February 22 would have qualified in any but an exceptionally disturbed month If March had been as disturbed a month as February there would have been no apparent sequence at all. If, as seems on the whole most probable, the above represents four recurrences of a single disturbance, the changes in duration and intensity that took place between the first and second occurrences were on a different scale from those that took place between the subsequent occurrences. A parallel, however, to the changes between the first and second occurrences is afforded by the completeness of the disappearance after the fifth occurrence

Another complex case is that presented by the long apparent sequence of eight disturbed days in 1895 to 1896, and the eight days immediately previous to them. The ranges, in millimetres, on these eight pairs of days were as follows, heavy type indicating that the day in question qualified as a disturbed day —

Dates	{	Dec 9 10	Jan 5 6	Feb 1 2	Feb 28 29	Mar 26 27	April 22 23	May 19 20	June 15 16
Ranges in mm	{	19 2 16 1	16 9 21 1	16·5 27 6	**88 9** **22·2**	**28 8** **25·0**	**27 0** 17 4	21 4 **26 6**	11 0 **22·2**

All the 16 ranges in the two lines were decidedly above the normal for their respective months, except 11 0 mm. on June 15. Thus the fact that the days in the second line show an unbroken sequence of eight disturbed days, while the longest sequence of disturbed days in the first line is only three, may be purely an accidental consequence of our restricting the selected disturbed days to five a month. Three ranges in the first line which did not qualify all exceed the first range in the second line which did. The successive pairs of days may well have represented repetitions of one and the same disturbance. If they did, then it probably presented at least 10 sequences, for November 12, 1895—i.e. the 27th day before December 9—qualified with a range of 25·1, and July 12, 1896—i.e. the 27th day after June 15—also qualified with a range of 23 4. On this view the climax would seem to have occurred on February 28, after three if not four previous appearances.

An analogous, though somewhat different, case is represented by the following pairs of days, extending from October 27, 1897, to May 5, 1898 —

Dates {	Oct 27 28	Nov 23 24	Dec 20 21	Jan 16 17	Feb 12 13	Mar 11 12	April 7 8	May 4 5
Ranges in mm {	7·0 16 8	3 5 14 5	80 9 17 3	17 0 20 3	19 1 9·0	23 9 16 0	20 9 10·1	22 8 16 7

As before, heavy type indicates that the day in question was a selected disturbed day   The last six entries in the first line represent a sequence of six disturbed days, commencing on December 20.   November 23, the 27th day prior to this commencement, was a selected quiet day, and had the smallest range of any of the quiet days of the month   Thus regarding the first line of figures alone, we would accept December 20 unhesitatingly as the first of the sequence   But while November 23 and October 27 did not qualify as disturbed days, the following did —October 29 with 18 7, October 2 with 19 6, and September 5 with 17 8, also November 25 had a range 10 1, considerably above the average   Thus October 28 and 29, November 24 and 25, and December 20 and 21 may represent sequences of a disturbance which originated at least as far back as September 5, but which had a recurrence period averaging a little under 27 days   On this view there may have been a repetition of the disturbance later than those shown, for May 30 qualified with 34 2   It is thus by no means improbable that there was in reality a sequence of 11, extending from September 5, 1897, to May 30, 1898.

The above examples will show the difficulty of saying which disturbances form sequences and which do not.   If instead of 5 we had taken 10 disturbed days a month, or had adopted some criterion which allowed a variable number averaging more than five, we should have found the difficulty greater.   Unless we can recognise some common trait in disturbances arising from what we may regard as a common ancestor, or obtain guidance from some allied branch of science, we shall probably find general statistical methods such as those adopted in the first part of the paper the safest to follow

The Growth of Metallic Eutectics.

By F. E. E. Lamplough, M.A., and J. T. Scott, B.A.

(Communicated by C. T. Heycock, F.R.S. Received June 6,—Read June 25, 1914.)

[Plate 9.]

Research on this subject originated in an attempt to discover in what way the structure of certain alloys is affected by undercooling at the first moment of solidification of the eutectic.

The formation around the primary crystals of an alloy of what may be called a halo or envelope of the second constituent, separating the primary crystals from the banded eutectic, has been considered by some workers to be the result of such superfusion. It has, however, been suggested by Desch that this effect is due to segregation of the eutectic in the immediate neighbourhood of the primary during solidification. At the same time it was suggested by him that, by preventing undercooling by means of inoculation, the influence of this phenomenon on the formation of such envelopes might be investigated.

The research at first followed two lines of investigation. Experiments were carried out to determine whether in different alloys the formation of such envelopes is always accompanied by appreciable undercooling and conversely. Further, examination was made of the effect of the prevention of superfusion by vibration or shaking and by inoculation with the secondary constituent.

In the investigation it was necessary to measure the temperature of the alloys by a method such that a rapid change of temperature was very quickly indicated by the thermometer, and further, that the mass of metal should be as nearly as possible of uniform temperature.

These conditions could only be realised by making the mass of the metal very small, the heat capacity of the thermometer inconsiderable and the conduction of heat from metal to thermometer as rapid as possible.

The alloys were investigated when possible in small test-tubes, $3'' \times \frac{5}{8}''$, which contained some 5 grm. of the metal. For temperatures below 600° C., copper-constantan thermo-couples were used, the two wires being fused together at the junction or brazed with silver solder. In such cases the thermo-couple was lightly smeared with a thin paste of "Purimachos" cement and water, which after drying contaminated the surface so that the wires did not alloy with the molten metal. The couple was very sensitive to rapid

changes of temperature of the metal, for the thin covering of the junction offered extremely little resistance to conduction of heat.

The moving coil of the galvanometer was provided with bifilar suspension to give a very short period of vibration, and experiments with pure metals, such as tin, showed that after considerable superfusion the temperature indicated by the instrument rose almost instantaneously at the first moment of solidification to a maximum value which remained constant during freezing. The temperature-time curves of the cooling alloys were recorded on a ground glass screen which moved vertically with uniform speed, whilst temperature was measured by the horizontal movement across the screen of a spot of light reflected from the galvanometer.

The tubes containing the metal were allowed to cool in an enclosure heated to a constant temperature, so that the rate of cooling and time of eutectic arrest could be readily varied as desired This enclosure consisted of a solid copper cylinder which was bored with holes of suitable size, one to hold the tube, wrapped with asbestos paper, the other to accommodate a mercury thermometer or thermo-couple The cylinder was wrapped with asbestos cloth and nichrome electrical heating coil, and was embedded in magnesia, the temperature being controlled to a small fraction of a degree by an arrangement devised by one of us.*

Investigations at temperatures above 400° C were carried out in a small resistance furnace similar to that described, 'Proc Camb Phil Soc,' 1911, p 175, the temperature measurements above 700° C being made with Pt, Pt-Rh couples protected by a silica tube, drawn out at the closed end so as just to accommodate the couple wires This alteration in the protection of the thermo-couple caused a considerable loss in the accuracy with which a rapid temperature change could be followed, but the arrangement was amply sufficient as a guide in " quenching " experiments

The research originated in observation of the considerable under-cooling at the first moment of solidification of eutectic which occurs when lead is the primary constituent in lead-tin alloys, attention was then turned to alloys of cadmium and tin in which primary crystals of cadmium are surrounded by very well marked envelopes. Investigations were later extended to many other pairs of metals

Attempts to connect the formation of these envelopes with the under-cooling of the alloys met with no success, for it was shown that such under-cooling was almost always produced when care was taken to prevent surface oxidation, and that whilst in some cases considerable superfusion existed without the formation of such structures, in others marked halos were

* To be described shortly to the Chemical Society.

accompanied by slight superfusion only. Moreover, when superfusion at the moment of eutectic formation was prevented either by inoculation or by shaking, the formation of the envelope was in no way affected

If such halos were produced at the first stage of eutectic growth, then the eutectic must have begun to grow from the primary crystals as nuclei It was therefore determined to ascertain, by quenching at an early stage of eutectic formation, whether or not this was the case. For this purpose a cooling curve of a given alloy was taken to determine on the recorder the exact temperature of the eutectic arrest, and its total duration , on repeating the experiment after the solidification of any desired proportion of the eutectic, the tube was withdrawn and plunged in cold water or melted paraffin wax

This method of investigation at once showed in the case of the cadmium-tin system that the eutectic growth did not originate at the primary cadmium crystals, and that the halo was only present round those primary crystals which had become enveloped by the growing eutectic Here the formation of the halo was certainly not connected with the sudden rise in temperature from undercooling at the first moment of formation of eutectic

Other cases in which the halo had been observed were investigated in this way, and it was very clearly shown that also in the cases of Pb–Sn, Ag–Cu, and Zn–Al, the halo was produced when the eutectic growth approached very close to the primary crystal The further solidification of the eutectic at this point consisted in the deposition of a layer upon the surface of the primary crystals of that constituent present as primary, the other constituent of the eutectic having solidified as an envelope surrounding the primary.

This method of investigation was at once recognised as giving valuable information on the character of the eutectic during growth, and research was prosecuted on these lines The formation of the eutectic during its growth was ascertained in the case of numerous pairs of components Some of these results were brought before the British Association, 1913, and a number of cases have since been investigated in which one constituent of the eutectic is an intermetallic compound From these investigations it has been possible to classify eutectics according to their character. The greater number of eutectics fall into two classes

1. Those of spherical radiating growth.

2 Those having well defined crystal contours, showing in section a herring-bone structure.

The eutectics of Sn–Pb, Sn–Cd, Zn–Cd, Ag–Cu, Zn–Al, Cu–Cu$_2$P, fall into Class I In all these cases *both* the constituents appear as primary crystals of rounded form. In the Zn–Cd system eutectic growth originates at primary

crystals of Zn, in the Sn–Pb system possibly at crystals of Sn ; in other cases, neither constituent present as primary serves as nucleus for the eutectic growth, *i.e* the eutectic growth may be said to be "independent" of both constituents.

In each case of spherical eutectic growth an envelope, or halo, was found to surround one of the constituents present as primary

A microphotograph of a Ag–Cu alloy containing copper crystallites as primary is shown in fig. 1. The alloy was quenched during the eutectic arrest and a spherical eutectic grain (the contour of which is necessarily slightly modified by the primary growth) is clearly outlined The primary copper crystals are rounded, and, where surrounded by eutectic solid at the moment of quenching, are enveloped with a continuous layer of the silver constituent

Among the second class of eutectics are those of Bi–Pb, Bi–Sn, Ag_3Sb–Sb, Au–$AuSb_2$, Mg_2Pb–Mg, Mg_2Sn–Mg, ZnSb–Sb, $NaCd_6$–Cd, $NaSn_2$–Sn

This class of eutectic was observed only in those systems which contained a constituent which solidified with definite crystal contour when present as primary. Though in most systems the other constituent was of rounded form, in no case was there segregation with production of an envelope surrounding a primary. In fact, such envelopes or halos have only been observed in conjunction with eutectics of Class I

In some cases the eutectic was "independent" of both primaries, in all other cases only those primaries of crystal shape were found to serve as nuclei or points of origin of the eutectic growth. In no system investigated during the research was the eutectic found to originate at the primary on both sides of the eutectic.

Fig 2 illustrates crystal grains of the eutectic Au–$AuSb_2$, quenched during growth

In a few systems, Bi–Cd, Cu_2Sb–Sb, SnAu–Sn, the eutectic is of a third type, neither spherical nor crystalline in contour, but of irregular form, somewhat resembling in shape a tongue of flame, projecting into the still molten mass In the cases investigated these were associated with one constituent crystallising as laminæ, and the eutectic growth very definitely originated at one of the primaries.

Fig. 3 illustrates an example of this type, in which the grains of Sb–Cu_2Sb eutectic are shown to originate at the plates of Cu_2Sb, whilst fig 4 shows the growth of the same eutectic to be independent of the primary crystals of Sb

The authors have endeavoured to repeat Vogel's experiment on the rapid cooling of a Zn–Cd alloy, but have failed to observe any such structure as is described by him.* In most of the systems investigated rapid cooling had

* 'Zeits Anorg Chem.,' vol. 76, pp. 431–432 (1912).

merely the effect of diminishing the scale of the eutectic structure. In a few cases, however, the rate of cooling exercised an influence on the nature of the eutectic. This was particularly the case with bismuth-tin alloys. With slow cooling—a eutectic arrest of half-an hour or more on masses of 5 grm.— the eutectic solidified as separate particles of the two metals, apparently without any relation to each other. More rapid cooling in air—eutectic arrest about one minute—gave a very well defined crystalline contour to the eutectic grains. On quenching the partly solid eutectic in either case, throughout the very fine ground-mass were found to be distributed small crystals of bismuth and much-branched crystallites of tin, the latter resembling the "quenched primary" crystals often observed in quenching from the liquid state an alloy containing excess of one constituent. In this case the regions adjacent to the eutectic grains were found to be devoid of these crystals. Somewhat similar "quenched primary" crystals have been observed in the case of alloys of cadmium and sodium, zinc and antimony.

The authors are about to investigate the viscosity of alloys, in order to determine whether this property is connected with the form of primary and eutectic growth.

A more extended account of the above work, with full microphotographs, will be presented at a later date.

Wave-lengths of Hydrogen Lines and Determination of the Series Constant.

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(Communicated by A Fowler, F R S Received June 11,—Read June 25, 1914)

Introductory

The Balmer or series spectrum of hydrogen possesses a special interest and importance for several reasons. In the first place hydrogen occupies a unique position among the elements, on account of its chemical properties and atomic weight. Secondly, the spectrum itself is notable as having been the first series to be recognised and represented by a formula, by Balmer in 1885. Many other series have since been found, but in no other case is the formula so simple in character or capable of representing the series with such great accuracy. Since Balmer published his "law" improved wave-lengths have been obtained by Ames, and the series has been greatly extended (in the chromospheric spectrum) by Dyson, Evershed, and Mitchell, but the formula remains completely satisfactory; that is to say, the observed and computed wave-lengths never differ by a greater amount than may reasonably be attributed to experimental error

From the above considerations it is clear that this spectrum cannot fail to offer a particularly attractive field for the work of the theoretical investigator who seeks to throw light on the mechanism of radiation The problem in the case of the hydrogen series is evidently reduced to its simplest terms; a satisfactory solution once obtained may, perhaps, be capable of extension to the series of other elements, for these series can all be represented by generalisations of Balmer's formula.

It thus becomes desirable to determine the wave-lengths of the lines in question with the utmost possible exactness with a view to testing the formula and making such modifications of it as may be found necessary. This was one of the objects in view when the present research was undertaken. Another was the evaluation on the International system of wave-lengths of the constant occurring in the formula, a number of considerable importance, since, as was shown by Rydberg, it may be used in all formulæ representing series of lines. Further, it was desired to find what degree of accuracy could be attained with the instrument available (a 10-foot concave grating), using the new International standards of wave-length. Finally,

the very frequent occurrence of the 'hydrogen lines in the spectra of vacuum tubes renders a precise knowledge of their positions very useful, as a check is thereby afforded on the results for other lines in the spectrum.

In connection with the first of the above objects, the testing of the formula, it may be pointed out that measurements of the first few lines of the series are, in all probability, all that are required For, supposing Balmer's formula to be found insufficiently exact, analogy with other series would require that a formula of the Rydberg type be tried, viz,

$$n = A - \frac{N}{(m + \mu)^2}$$

Since Balmer's law is such a very close approximation, μ must be very small and A very nearly equal to $\frac{1}{4}N$. Now the effect of μ upon the wave-length, or $d\lambda/d\mu$, varies as $\lambda^2/(m+\mu)^3$, and hence decreases very rapidly in the direction of the limit Thus, for example, the value of $d\lambda/d\mu$ is 54 times as great for $H\alpha$ as for $H\zeta$ It is evident then that if the value of μ is in question the data are to be obtained from the first few lines of the series, so that the above-mentioned results of Dyson, Evershed, and Mitchell, although capable of furnishing a fairly good value for N, are in this particular connection very little advance on those of Ames.

A summary of the wave-lengths hitherto determined is given in Table V below. It will be seen that the deviations of the observed values from those computed amount at times to as much as 0 05 Å.U., so that there seemed to be room for a substantial increase of accuracy. Exactly what degree of precision was attainable by the means employed in the present investigation was not known when the work was commenced—certainly not more than 0 001 Å.U It is thought that this limit has very nearly been reached, at any rate in the case of the four lines γ, δ, ϵ, and ζ

Conditions of Experiment.

The source of light throughout was a hydrogen vacuum tube (of the ordinary Plücker form) excited by means of a 12-inch coil. A motor break was used in conjunction with the latter, and the primary current was usually between 2 and 4 ampères. The capillary portions of the various tubes ranged between 0·1 and 3 mm. in bore, and the pressures employed were from ½ to 5 mm A number of experiments were made with a view to determining the most suitable conditions for the purpose. The condensed discharge was out of the question, for although it gives a very pure series spectrum, suppressing the secondary or compound line spectrum, the lines are much too broad for accurate measurement except at very low pressures, when the luminosity

becomes very feeble   With the uncondensed discharge a bright series spectrum is obtainable from the capillary, but the secondary spectrum is also present.   The relative brightness of the latter can be diminished by increasing the current density—most conveniently effected by using a narrower capillary —but it is not practicable to carry this process beyond a certain limit, owing to the broadening of the lines which results   This broadening effect increases with the order of the line, so that for the higher members of the series it was impossible to use such a high current density as was practicable for $H\alpha$.   In the latter case the tube could be made so brilliant that an exposure of one minute was sufficient, whereas in order to obtain the sixth member, $H\zeta$, six hours was the minimum necessary, even when using the fastest plate obtainable   The light from the middle portion of the capillary was utilised, the observations being made perpendicular to its length   Ames appears to have used an end-on form of tube, but this method is open to objection on account of the marked development of the secondary spectrum which always occurs at the ends of the capillary   As this is associated with an actual diminution in the intensity of the Balmer series, the advantage of viewing the capillary axially is less than might appear, when, as in the present case, the spectrum obtained is astigmatic, so that there is no advantage in concentrating the light into a small image, the method described above is preferable

The hydrogen was prepared by electrolysis of a saturated solution of carefully purified barium hydroxide which was very kindly supplied by Prof. H. B Baker, F.R S   The spectrum of the gas so obtained showed no impurity except a slight trace of oxygen, which seemed to be derived from water vapour, as it was not present when the gas had been passed over anhydrous phosphoric pentoxide   This was not done, however, as the intensity of the series is greatly diminished thereby, and that of the secondary spectrum increased.   Hydrogen which has been very thoroughly dried by standing over P_2O_5 for some time gives a comparatively feeble Balmer series, It was also noticeable that the relative brightness of the series lines tended to decrease after the discharge had been passing for some time   With the heavier currents used this falling off was very appreciable in a quarter of an hour or so, and necessitated the refilling of the tube with fresh hydrogen. The repetition of this process being rather troublesome during long exposures, an apparatus was constructed by means of which a continuous flow of hydrogen could be maintained.   The gas was passed from the generator into a reservoir having a capacity of about a litre and then into the vacuum tube through a length of very fine capillary tubing.   The other end of the vacuum tube was connected to the Gaede pump, which was kept working all the time, through a short piece of capillary tubing of medium bore.   The apparatus

proved very convenient, and enabled the brightness of the series lines to be maintained unaltered for as long as desired   It was only necessary to recharge the reservoir once in several hours, when the pressure in the discharge tube was getting rather too low.   This method of working possesses another advantage, in that the flow of hydrogen quickly removes the carbonaceous gases which are always given off when the discharge is first passed. After a few minutes' running the Ångstrom bands completely disappeared, and were not seen again

Determination of Wave-lengths

The photographs were taken in the second and third orders of the 10-foot concave grating of the Royal College of Science   A description of the mounting, which is on the Littrow plan, has been given by Eagle [*] A variety of plates were used, according to the wave-length and intensity of the line to be photographed   The following Table gives some details :—

Table I.

Line	Plate usually employed	Average exposure
α	Wratten Panchromatic B .	7 minutes
β	Imperial Ordinary	40 „
γ	„ „	80 „
δ	Wratten Drop Shutter	100 „
ε	Lumière Violet Label	5 hours
ζ	„ „ „	6½ „

The iron arc used to give the comparison spectrum was about 6 mm long and carried a direct current of about 5 ampères, obtained from the 110-volt mains.   The electrodes were about 1 cm in diameter   The light from the whole of the arc was utilised, the electrodes only being screened off from the slit.

The comparison shutter of the instrument permits of the juxtaposition of three spectra.   Accordingly, the hydrogen spectrum was put in the middle, with iron arc comparisons overlapping above and below.   One arc spectrum was exposed before the hydrogen, and the other after   The two were measured and reduced separately, so that any shift of the plate or grating during the exposures was immediately evident from the discordance of the two results.   When the exposures are long it is quite necessary, as will be seen later, to have such a check on the stability of the instrument.   The Hilger micrometer used for the measurements had a screw of 1 mm. pitch and 150 mm in length.   Its errors were investigated and corrections applied, but these were so small as to be hardly appreciable in the majority of cases.

[*] 'Astrophys. Journ.,' vol. 31, p. 120 (1910).

The scale of the spectrum is about 2 6 Å.U per millimetre in the second order, and 1 7 Å.U. per millimetre in the third order   Over a range of not more than 15 Å U wave-lengths may be calculated from micrometer readings by means of a linear formula , if the range is greater than this, a correction, which is approximately parabolic in form, must be applied   For a range of 100 Å.U the correction at the centre is of the order of 0 1 Å U , so that for this type of mounting it is particularly desirable to use standard lines as close together as possible   The secondary International standards, averaging 50 Å.U. apart, are much too few and far between   The publication of tertiary standard wave-lengths by Burns* was therefore very welcome, and his results were of the utmost service   In the early part of the work some six or eight iron lines were employed for each reduction, with a view to checking the internal agreement of Burns' values   This was found to be so uniformly satisfactory that it was judged permissible, in order to lessen the labour of measurement, to rely upon a somewhat smaller number, usually four or five, but never less than three   The measurements were made with the greatest care , six independent sets of readings were taken on each line, the plate being reversed end for end after the first three   The final mean readings, after correction for micrometer errors, were reduced to wave-lengths with the help of an arithmometer, and a curve of corrections constructed if necessary

Two difficulties were encountered in the wave-length determinations First, the measurement of the hydrogen lines was by no means easy, on account of their width.   This averaged about 0 25 Å U for α, 0·15 for β, and 0·17 for γ, δ, ϵ, and ζ, very much more than that of an ordinarily good iron line   Second, the results derived from the two comparison spectra were often seriously discordant.   This was a very fruitful source of trouble—the various attempts which were made to locate its origin occupied, in fact, most of the time spent on the research   These discrepancies were small, only reaching 0·04 Å.U. in two cases, but quite certainly existed, that is, they could not be attributed to errors of measurement.   Further, they were most marked in the case of long exposures, a point of some significance.   Thus the determination of β and γ was practically free from trouble of this nature. The case of α will receive separate consideration.

Sources of Error

It is perhaps worth while to summarise the chief sources of error in connection with wave-length determinations by this method—

* 'Zeitschr. f. Wiss. Phot.,' vol. 12, 6, p. 219 (1913); 'Lick Obs. Bull.,' vol. 8, No. 247 (1913).

(1) Incomplete illumination of the grating.

(2) Curvature, or other irregularity of the slit (only effective in astigmatic instruments)

(3) Unevenness of plate surface (only effective when diffracted beam does not fall normally on plate).

(4) Relative displacements of slit, grating or plate, whether arising from—

(*a*) Mechanical disturbance ; or

(*b*) Temperature change.

(5) Change of refractive index of air, arising from variation of temperature or pressure

(6) Inaccuracy of setting on lines, systematic and otherwise

(7) Inaccuracy of micrometer screw, including such as may result from temperature variations during the measurement

(8) Incorrect values for the standard wave-lengths used.

Since the discrepancies in question were so small, although large enough to be of importance for the present purpose, and since only the first two of the above possibilities could be absolutely removed, it will be understood that it was a matter of some difficulty to detect the source of the trouble Complete illumination of the grating was secured in the usual manner, by using in each case a lens (of sufficient aperture) to form an image of the source on the slit   The influence of the shape of the slit was quite easily eliminated by using the same portion of the latter for all three exposures.   With regard to the influence of the plate surface it may be pointed out that, on the average, displacements of this kind would be just as likely to occur to the iron as to the hydrogen lines, in fact, more so, since more of the former were measured.   In point of fact, however, no shifts of any consequence were encountered in the case of the iron standards used Moreover, an examination of the plates failed to reveal any correspondence between poor surface and discordant results.   The changes of wave-length produced by variations in atmospheric temperature and pressure are of the order of $0\,005$ Å U. per $1°$ C. and $0\cdot002$ Å.U. per millimetre respectively. The former source of displacement was always negligible in the present instance, and it was only in a very few cases that the pressure shift was large enough to be worth taking into consideration.   After allowing for it, if necessary, there still remained a number of serious discrepancies to be accounted for   As far as the measurement was concerned, systematic errors of setting should be eliminated, assuming constancy of personal equation. Accidental errors of setting were unavoidable, of course, but after some experience it was quite possible to form a rough estimate of their probable magnitude.   For example, in the case of a good plate an accuracy of about

0·002 Å.U was to be expected in setting on an average iron line. The uncertainty was always larger for the hydrogen lines, and varied greatly with their breadth and diffuseness The permanent errors of the micrometer were investigated and allowed for In order to guard against the effect on the screw of varying temperature three separate sets of settings were made, as already mentioned. The discrepancies in question could hardly have been due to variations in wave-length of the iron lines, the conditions under which they were produced (length of arc, current, etc.) were kept as constant as possible throughout the experiments, and the practice of measuring a number of lines furnished a further safeguard against individual shifts

There remains to be considered the possibility of disturbance of the spectrograph. The mounting of the College instrument would appear to possess sufficient stability to render accidental shifting of either slit, grating or plate very unlikely, especially as it rests on piers which are independent of the floor of the laboratory The uniformly concordant results in the case of the shorter exposures were reassuring on this point Further, several long exposures were taken during the night, using every conceivable precaution against disturbance of the instrument, but without securing perceptibly better results. Variation of temperature would appear to be a much more likely origin of the trouble. Taking 0·00002 as the coefficient of expansion of the speculum metal, we find that in the neighbourhood of Hζ ($\lambda = 3889$) a shift of 0 02 Å U. (such as not infrequently occurred) will result if the temperature of the grating changes by 0 26° C. between the two iron exposures. Thus in order to preclude variations of more than 0 002 Å U, the smallest which can be detected in the present case, it is necessary that the temperature shall remain constant to within 0 03° C. To test the point a platinum thermometer was employed It was of the grid type, and was placed above the grating and as close to it as possible A continuous record of the temperature, on a scale of 1 inch to 1° C, was obtained by means of a Callendar recorder It was found that temperature variations of sufficient magnitude to account for the observed shifts did undoubtedly occur, and an attempt was made to correlate the two, but without much success In several cases there was an approximate correspondence, but usually there was not. But for several reasons it did not seem feasible to make a really satisfactory investigation of the point at issue. For one thing the hydrogen lines, as already noted, are broad and increasingly diffuse towards the limit of the series. Hence, so far as the first six lines are concerned, the probable error of measurement is greatest for ϵ and ζ, which on account of their feeble intensity require the longest exposures and are thus most susceptible to the effects of varying temperature Moreover, it was not

usually possible to measure satisfactorily more than one line of the series on one plate, since its neighbours were on the one side over- and on the other under-exposed Thus the determination of the shift depended entirely on one line, a very unsatisfactory state of affairs It is hoped to resume the study of the question under more favourable conditions, that is to say in connection with a spectrum containing a number of fine lines

Whether or not the displacements found in the present case are to be ascribed to temperature changes, it is certainly likely that the latter will provide a serious obstacle to the accurate determination of wave-lengths when the exposures are long The instrument employed is very compact, being entirely contained in a box 11 feet by 2 feet by 2 feet, the walls of which are double, with a lagging of slag wool between One would thus expect the temperature to remain much more nearly constant than in the case of other forms of mounting, *e.g* Rowland's, so that it will be interesting to compare the present results with those obtained with other instruments under similar circumstances.*

It was particularly desirable, for the reasons already explained, to determine the position of Hα with the utmost accuracy Unfortunately, however, the probable error of this result is larger than that of any of the other five lines measured This is in part due to the scarcity of standard lines in the region in question, only four being available,† and those some distance apart Using the first and last for the derivation of a linear formula, the curve of corrections obtained from the other two departed very appreciably from the parabolic form which holds for shorter ranges. A cubic formula was accordingly used to determine the correction required for Hα In addition to this source of uncertainty some evidence was obtained of variability of the wave-lengths of these standards The possibility of such variations is also suggested by the rather large discrepancies between the values obtained for these lines by different observers.‡

Wave-length Results

In combining the results for any one line the two values derived from each plate were weighted according to the agreement between them, if they

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* Since the above was written, a paper which bears on the point has come to hand (R. T Birge, 'Astrophys. Journ,' vol. 39, p 50 (1914)) The author was investigating the first positive band system of the nitrogen spectrum, and the exposures were very long (up to 120 hours) He found shifts in exact correspondence with the observed temperature changes, but he was able to control the latter (the grating being mounted in a specially constructed room) in such a way as to neutralise the disturbing effects of variations of atmospheric pressure.

† 6494 991, 6546 247, 6592·925, 6678 600.

‡ Burns, *loc. cit.*

disagreed by more than 0 02 Å.U. both were rejected.   The probable errors given have been derived by means of the usual formula, viz ,

$$p e = \pm 0.6745 \sqrt{\frac{\Sigma(pvv)}{(n-1)\Sigma(p)}}.$$

It may be remarked that in the case of Hα the probable error stated is too small, since it does not include the uncertainty arising from the causes mentioned above

The results are summarised in the following Table :—

Table II

Line	Number of results	Number of standards used	λ (I A)	p e
α	10	4	6562 793	±0 0017
β	18	6	4861 326	±0 0010
γ	9	6	4340 467	±0 0006
δ	14	10	4101 738	±0 0018
ε	10	11	3970 075	±0 0016
ζ	12	15	3889 051	±0 0011

These wave-lengths were reduced to vacuum by applying corrections taken from Kayser's ' Spectroscopie,' vol. 5, p 514   If now Balmer's law is accurately obeyed the value of N given by the expression

$$\frac{10^8}{\lambda} = N \left(\frac{1}{4} - \frac{1}{m^2} \right)$$

should be the same for each line within the limits of observational error. The figures given below appear to indicate that such is not the case.

Table III

Line.	m.	λ (vac)	π (vac)	N.	p e
α	3	6564 574	15,233 281	109,679 62	±0 08
β	4	4862 659	20,564 880	36	±0 02
γ	5	4341 664	23,082 644	26	±0 02
δ	6	4102 873	24,373 165	24	±0 03
ε	7	3971 176	25,181 458	24	±0 04
ζ	8	3890 181	25,706 075	25	±0 08

A small systematic departure from Balmer's law is obviously suggested, the nature of the deviation being such as to point to a Rydberg formula as being preferable   Before calculating such a formula, however, a careful examination of the value for Hα was made, in order to make sure that the deviation in question could not reasonably be attributed to error in the derived wave-length.   The effects of errors of measurement and method

2 x 2

of reduction of the standard wave-lengths and of the correction to vacuum were considered, and an estimate formed of the maximum total error on all these accounts. This seemed to be about 0 012 Å U in the extreme and very improbable case when all the errors have the same sign. To fit Hα to a Balmer formula derived from the other lines requires a correction of about 0 022 Å U, so that one is forced to the conclusion that the deviation is genuine.

Duplicity of the Hydrogen Lines.

The determination of an exact formula for the Balmer series is unfortunately complicated by the fact that the lines are very close doublets, so close, indeed, that they appear single on all the plates obtained in the present work, except that Hα has shown a suggestion of resolution in a few cases. Michelson applied his interferometer to α and β in 1892 and found them to be double, the separations being 0 14 and 0 08 Å U respectively, but the components were so broad as to render the resolution very difficult The lines have since been examined by a number of observers with very varying results There is a general consensus of opinion that α and β are double, but considerable disagreement as to the precise separations of the components. Thus for α Houstoun[*] gives 0 065 Å U, Fabry and Buisson[†] 0·132, and Paschen and Back[‡] 0·20 Further, the components appear to be unequal in intensity, the less refrangible being slightly the stronger[§] (the ratio is given by Michelson as about 10 · 7)

There is thus some uncertainty as to what point of the compound line the present measurements really refer, it will presumably be slightly to the less refrangible side of the point midway between the components. In any case it seems evident that the simple Balmer formula is not exact when applied to the " centre of gravity " of the lines, although there is just a possibility that it may hold for the less refrangible components. An attempt was made to derive wave-lengths for the components and calculate separate formulæ for them, but the data available seem too uncertain to permit of reliable results being obtained in this way.

Corrected Formula for Hydrogen Series.

The general formula of Rydberg is as follows :—

$$n = \frac{N}{(2+p)^2} - \frac{N}{(m+\mu)^2}.$$

[*] 'Phil. Mag,' (6), vol. 7, p. 456 (1904).
[†] 'Journ. de Phys,' June, 1912.
[‡] 'Ann. d. Phys.,' vol. 39, p. 897 (1912).
[§] Fabry and Buisson, loc. cit.

As the deviation from the Balmer or single constant formula is so small, it is natural to try next if the observations can be fitted by means of a modified Rydberg formula containing only two constants   If μ is put $= 0$, a least squares solution gives $N = 109,678\ 82$ and $p = -\ 0\ 0_5 36$ This formula (II) represents the lines within $0\ 002$ Å.U , with the exception of Hα, which it gives $0\ 006$ too high   It is distinctly preferable, however, to put $p = 0$, as the formula (I) then gives a fit quite within the limits of experimental error   The values obtained for the constants by the method of least squares are

$$N = 109,679\ 22, \qquad \mu = +\ 0\ 0_5 69$$

Table IV

Line	λ observed	p e.	λ calculated.	O — O
α	6562 798 I A	±0 0017	6562 7929	+ 0 ·0001
β	4861 326	±0 ·0010	4861 3266	— 0 ·0006
γ	4840 467	±0 ·0006	4840 4661	+ 0 ·0009
δ	4101 738	±0 0013	4101 7376	+ 0 ·0004
ε	3970 ·075	±0 ·0016	3970 ·0748	+ 0 ·0002
ζ	3889 051	±0 ·0011	3889 ·0516	— 0 ·0006

A comparison of the results of observation with the two formulæ is given in the figure.   The ordinates represent the difference between a standard value of N (109,679 22) and the value derived from each line by assuming Balmer's law   The superiority of the formula adopted is clearly shown in spite of the smallness of the wave-length deviations.
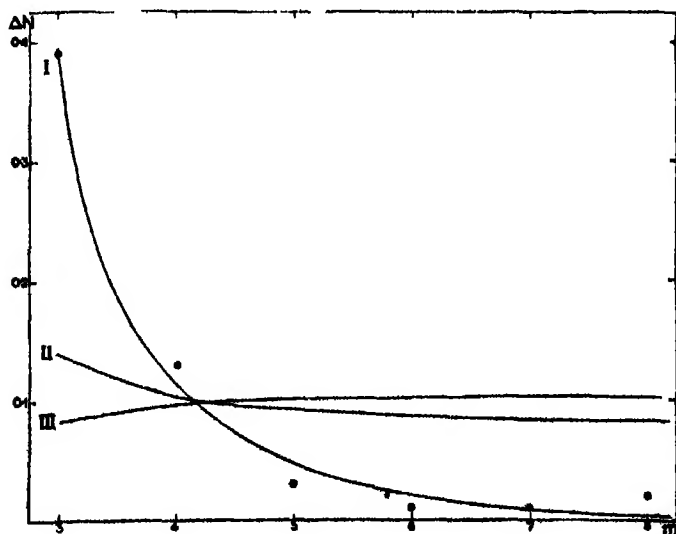
The figure also gives the results obtained by means of a formula (III) suggested by Dr Bohr in a letter to Prof. Fowler, viz :—

$$n = N\left(\frac{1}{4}-\frac{1}{m^2}\right)\left\{1 + k\left(\frac{1}{4}+\frac{1}{m^2}\right)\right\}$$

The departure from the simple Balmer formula, which has already been derived theoretically by Dr Bohr,[*] depends upon a correction of the mass of the electron due to its velocity   It would seem that this formula is not of a suitable type to represent the experimental results.

The calculation of a general Rydberg formula gave the following results ·—

$$N = 109,679\ 23, \qquad \mu = +0.0_570, \qquad p = +0\ 0_78$$

The improvement obtained by introducing the third constant p is so small as to be scarcely perceptible, even when the fourth decimal place (in wavelengths) is taken into account.   It will be noted that the values of N and μ are practically the same as before, while p is exceedingly small   It thus seems quite legitimate to adopt the two-constant formula already given

With regard to the constants N and μ, it seems pretty certain that the former must lie somewhere between 109,679 20 and 109,679·25   The value of μ cannot be relied upon with such confidence, as it depends almost entirely on the wave-length of $H\alpha$, which is rather more doubtful than the others. But μ is certainly positive, and very probably lies between 0 0_53 and 0·0_410.

The above formula gives the convergence frequency of the series as 27419 805, corresponding to a wave-length (in air) of 3645·981 I.A , or 3646 125 on Rowland's scale.

Comparison with other Observations

The following Table gives a comparison of the wave-lengths calculated from this formula with the results of various observers.   The former values refer to air at 20° C. and 760 mm., and the latter have been reduced to the International scale.

The observations of Dyson, Evershed, and Mitchell were made on the chromosphere during total solar eclipses, the two former employing prismatic instruments and the latter plane and parabolic gratings.   As the pressure in the upper chromosphere must be very low, we should expect the wave-lengths of the hydrogen lines to be practically identical with those determined from vacuum tube work.   The results of Dyson and Evershed support this view,

*   *   *

[*] 'Phil. Mag.,' vol. 26, p. 1 (1913).

Table V

m	Calculated λλ (I A)	Observed – calculated.				
		Rowland *	Ames †	Dyson ‡	Evershed §	Mitchell ‖
3	6562 793	+0 029	+0 02			
4	4861 327	+0 021	−0 02		+0 06	+0 39
5	4340 466	+0 005	+0 03		−0 10	+0 54
6	4101 788	+0 110	−0 04	+0 03	+0 11	+0 11
7	3970 075		+0 03	−0 01	+0 11	+0 26
8	3889 052		−0 05	−0 05	−0 05	+0 27
9	3835 386			−0 01	−0 03	+0 15
10	3797 900			+0 01	−0 05	+0 10
11	70 682			+0 01	−0 05	+0 12
12	50 154			+0 03	−0 02	+0 12
13	34 370			+0 01	+0 02	+0 17
14	21 940			−0 03	−0 10	+0 12
15	11 973			+0 01	+0 02	+0 09
16	03 855			+0 01	+0 02	+0 04
17	3697 154			0 00	−0 01	+0 06
18	91 556			0 00	0 00	+0 08
19	86 633			+0 03	−0 01	0 00
20	82 809			−0 03	−0 01	+0 01
21	79 354			+0 01	+0 03	−0 01
22	76 364			+0 04	+0 01	−0 02
23	73 761			0 00	−0 03	+0 06
24	71 477			−0 16	−0 09	−0 17
25	69 466			−0 03	−0 06	−0 01
26	67 683			+0 07	+0 01	+0 09
27	66 096			−0 03	+0 01	−0 01
28	64 679			−0 04	−0 06	−0 02
29	63 405			+0 03	0 00	+0 02
30	62 357			−0 05	−0 04	−0 08
31	61 220			−0 01	−0 05	+0 06
32	60 279					+0 05
33	59 422					
34	58 640					+0 02
35	57 925					+0 12
36	57 269					−0 01
37	56 665					−0 01

* Preliminary Table of Solar Wave lengths
† 'Phil Mag,' (5), vol 30, p 33 (1890)
‡ 'Phil Trans,' A, vol 206, p 403 (1906)
§ 'Phil Trans,' A, vol 201, p 457 (1903)
‖ 'Astrophys Journ,' vol 38, p 407 (1913).

while those of Mitchell might at first sight appear to be opposed to it. The average deviations are as follows*:—

Dyson	. .. ...	(O ∽ C) = 0 020,	(O − C)	=	−0·000
Evershed	....	„ = 0 035,	„	=	−0·014
Mitchell	. ..	„ = 0 105,	„	=	+0·100

There is thus a considerable systematic deviation in the case of Mitchell's

* Neglecting Nos. 22, 24, 28, 32, 33, 35, which, according to Mitchell, are blended with other lines.

results, but nothing to correspond with this in the other two cases   The explanation probably lies in the difficulty of determining wave-lengths from objective or slitless spectra such as these   This difficulty is especially marked in the case of strong lines   Since Mitchell's list contains many more lines than either of the other two it is to be presumed that his hydrogen lines are stronger, and hence more difficult to measure   It will be seen that the discrepancies are particularly large for the earlier (*i e* the strongest) members of the series, as would be expected on this view

Series Relationships in the Hydrogen Spectrum.

It is frequently possible in work on series to obtain valuable evidence with regard to the one under discussion from an examination of the series associated with it   For example, if the Rydberg-Schuster relations hold— and they are exceedingly nearly exact, if not absolutely so—the convergence frequency of the Diffuse series is equal to the "variable part" of the first Principal line.   It may readily happen that the latter, on account of its strength, sharpness or position in the spectrum, is better suited to accurate investigation than the Diffuse lines themselves, so that it may be practicable to obtain in this way a better formula than is derivable merely from internal evidence   It is unfortunate that in the present case no assistance of this kind is available, on account of the special character of the hydrogen spectrum

Up to the present the Balmer series has usually been regarded as of the Diffuse type.   In 1896 Pickering found a series of lines in the spectrum of ζ Puppis, which it was quite natural to conclude was the associated Sharp series.   There was, of course, the anomaly that it could not be obtained in the laboratory, but the numerical evidence of identification seemed so strong as to outweigh this objection.   The case seemed to be further strengthened by Rydberg's well known calculation of the stellar line 4688 as the first line of the Principal series, and to be finally established by Prof Fowler's success in producing this line, together with several other members of Rydberg's calculated series, in the laboratory   Prof Fowler's most recent work* on series of enhanced lines, however, seems to leave no room for doubt that both the " ζ Puppis " and the " 4688 " series are really enhanced line series of helium   The same conclusion had previously been reached from theoretical considerations by Dr Bohr (*loc. cit.*).

The hydrogen spectrum thus regains its apparently anomalous position, and we are led to enquire whether the Balmer series is really a Diffuse series, and, if so, what has become of the associated Sharp and Principal

* Bakerian Lecture, 1914, 'Phil Trans.,' A, vol. 214.

series   The evidence as to the nature of the Balmer series is very meagre.
The fact that the less refrangible component of Hα is the stronger favours
the view that the series is of the subordinate type.   The diffuse character of
the lines naturally suggests the Diffuse type, but this is by no means an
infallible criterion   The electrical resolution of the lines appears to
correspond with that of the Diffuse series of helium   There is no further
evidence available at present—the Zeeman effect, for example, throws no
light on the matter

Let us suppose, however, that the series is of the Diffuse type   Analogy
with all other known cases leads us to expect that the Sharp series will be
developed under precisely the same conditions of experiment, and, since it
must have the same convergence frequency as the Diffuse, the lines will fall
in the same region of the spectrum, so that they should be readily observable
As they have never been seen, however, it is reasonable to suppose that in
the case of hydrogen the Sharp and Diffuse series practically coincide,[*] the
Balmer series representing the superposition of the two   There is not at
present any direct evidence bearing on the question, but the above manner of
regarding the Balmer series has the advantage of bringing the hydrogen
spectrum into line with other series spectra, and converting it from an
exception into a limiting case.

If this view is correct, we should expect the Principal series to be given
either by $n = N/2^2 - N/m^2$, or by $n = N/1^2 - N/m^2$, the ambiguity arising
from the very small value of μ in the Balmer series.   In the former case the
Principal would be superposed on the two Subordinate   In the latter we
have the series recently obtained by Lyman in the Schumann region
Similarly, the Fundamental series would be given either by $n = N/3^2 - N/m^2$
or by $u = N/2^2 - N/m^2$ respectively   The former series is in the infra-red ,
two of the lines ($m = 4$ and $m = 5$) have been obtained by Paschen

The question of the precise nature of the Balmer doublets must be left
unsettled for the present.   Hα and Hβ are the only members which
have been resolved, and the results obtained are so discordant that no
conclusion can be drawn from them   Bohr[†] makes the interesting
suggestion that the lines are normally single, but are resolved into doublets
under the action of the electric field in the vacuum tube   If this were so
the discordance of the results of various workers would be very simply
explained, as arising from differing conditions of experiment   But for any
one case the ratio of the separations of Hα and Hβ should be 0·69, taking
Stark's results for these lines.   Paschen and Back's measurements give

* In some other cases they lie very close together, e.g., for K
† 'Phil Mag.,' (6), vol. 27, p. 506 (1914).

0·83 for this ratio, in sufficiently 'good agreement with the above. On the other hand, Michelson's results give 1·75 and Fabry and Buisson's 1·83, so that it does not seem possible to account for the discrepancies in this way.

Summary

1 The wave-lengths in I A. of the first six lines of the hydrogen series have been determined with an accuracy of about 0 001 Å U.

2 Balmer's formula has been found to be inexact   The results may be represented by a modified Rydberg formula containing only two constants, thus —

$$n = \frac{N}{4} - \frac{N}{(m+\mu)^2},$$

where $N = 109,679\ 22$ and $\mu = +0·0_569$

3. An accuracy of 0 001 Å.U. is attainable in the third order of a 10-foot concave grating if the exposures are short (say less than half an hour). With longer exposures accurate determinations become very difficult if the temperature of the instrument cannot be controlled

4. The tertiary iron arc standards determined by Burns were tested in the special regions under investigation, and found very satisfactory   .

On the Measurement of Alternating Electric Currents of High Frequency.

By Albert Campbell, B A , and D. W Dye, B Sc.

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(From the National Physical Laboratory.)

[Plate 10]

Both from the scientific and practical point of view the accurate measurement of alternating current, voltage and power at high frequencies is of considerable importance   For example, in the domain of pure science the study of energy losses in dielectrics at high frequencies is most interesting, while on the practical side, in radiotelegraphy, there is a wide field for improved methods of measurement.   At frequencies from 100,000 to 2,000,000 $\sim$ per second by the methods at present in use it is comparatively easy to measure currents of the order of 0 1 ampère, but many difficulties present themselves when we have to deal with currents of 1 to 50 or 100 ampères   We have recently investigated several ways of measuring these larger currents, and the object of the present paper is to give a description of the more satisfactory methods and the results obtained by them

Thermal Instruments—The most common method of measuring a high frequency current is to pass it through a conductor and observe the rise of temperature of this as shown by its expansion or change of resistance, or by means of one or more thermojunctions in contact with it or near it   The last method, that of a heater and separate thermopile, was investigated by one of us many years ago* and was used later† to measure the voltages induced in small search coils by alternating magnetic fields.   The separate heater system was used by Mr Duddell‡ in his beautiful application of Mr Boys's radiomicrometer to current measurement , and his thermo-galvanometer still represents the high-water mark in efficiency   While, however, the self-contained thermojunction and moving coil no doubt give the highest efficiency, the use of a thermopile connected to a separate galvanometer has several advantages, especially in laboratories where economy of instruments has to be considered.   A variety of heaters and thermopiles can be used with

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* A. Campbell, 'Roy Soc. Edin Proc.,' July, 1687, p 406.

† A Campbell, 'Phil Mag,' Jan , 1899, p 2

‡ 'Phil. Mag , vol. 8, p. 91 (1904).

a single galvanometer, and both the sensitivity and the promptness can usually be altered within pretty wide limits by adding resistance to the galvanometer circuit.

The thermopiles we used in general consisted of from four to ten pairs of thin wires about 0·1 mm diameter and 1 cm long   The combinations used were various, but most frequently either iron-constantan or manganin-constantan.   The iron-constantan couple has two strong points in its favour, it gives a voltage almost exactly proportional to the difference of temperature, and the temperature coefficient of its voltage sensitivity is very small   On the other hand, the high thermal conductivity of the iron is not desirable, and, as will be explained later in this paper, its magnetic properties may give trouble   It was for these last two reasons that in many of the experiments manganin-constantan couples were used instead   Perhaps the most commonly used thermal ammeter consists of a single thermojunction in metallic contact with a heater wire.   In our experience this is not nearly so good as the separate heater system   When the galvanometer circuit is in metallic connection with one point of the high frequency circuit, usually a small high frequency current will pass to the galvanometer due to the capacity to earth of the galvanometer and its leads, and this current may often cause a change of deflection by heating one of the thermojunctions.   It is often possible to obtain a deflection of the galvanometer when only one terminal of the heater is connected to the high frequency circuit   These troublesome effects cannot be got rid of by screening the galvanometer or earthing a point of the circuits, but the use of a separate heater gives in general a complete cure.   Accordingly, in all that follows, unless the contrary is stated, it will be understood that the heater is completely insulated from the thermopile and galvanometer circuit   When such a heater is used, the instrument can be calibrated with direct current, which is not always possible with instruments that have the thermojunction in metallic contact with the heater   In general, if the ammeter is to be accurate at different frequencies, the heater should be of such form and dimensions that its effective resistance shall remain appreciably constant throughout the range of frequencies used.   This condition is usually attained by making the heater of sufficiently thin wire; a uniform tube of very thin wall would be another possible form.   A convenient table has been given by Austin[*] showing the maximum permissible diameters of wires of various metals for 10 per cent, 1 per cent. and 0·1 per cent. variation in effective resistance at various frequencies.   The resistance of a constantan

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[*] Austin, 'Jahrbuch der Drahtlosen Telegraphie,' vol 6, p. 588 (1913).   See Zenneck, 'Leitfaden der Drahtlosen Telegraphie,' p. 352.   J H. Dellinger, 'Bulletin of Bureau of Standards,' vol. 10, p. 92 (1913).

wire of 0·15 mm. diameter increases less than 1 in 1000 at a frequency of $3 \times 10^6 \sim$ per second ($\lambda = 100$ mm), the change in similar wire of 0 30 mm. diameter is less than 1 per cent   The use of more than two wires in parallel, in order to permit the measurement of larger currents, presents difficulties,* since exact symmetry is not easily secured.   Most of the heaters we have used were of short lengths (straight, crinkled, or doubled back on themselves) of constantan wire of diameters ranging from 0 04 to 0 3 mm.   The thickest of these wires will not stand more than 3 5 ampères in air, and of course, for proper working, could not be used for currents so large as this   We have found, however, that the larger currents can be dealt with by immersing the whole combination of heater and thermopile in a large vessel of liquid such as paraffin oil †

Oil-cooled Heater —The behaviour of a separate heater and a thermopile immersed in oil is very interesting   The difference of temperature indicated by the thermopile depends not only upon the positions of the opposite junctions relative to the heater, but also upon the thermal expansibility, the viscosity and other properties of the liquid   When the thermopile and the heater wire are both placed horizontal in the liquid, with one set of junctions above but projecting slightly beyond the heater, the readings of the galvanometer are in general by no means proportional to the square of the effective current in the heater, as they would approximately be if the surrounding medium were only air   The relative positions of the heater and junctions can be adjusted by trial, so that over a large range of current the galvanometer deflections shall be almost exactly proportional to the current   This unexpected result is very useful, as an almost uniform scale is so much superior to the square law scales of all previous thermal instruments‡   A typical example is given in Table I, which refers to a heater of 0 25 ohm resistance immersed to a depth of 8 cm. in paraffin oil of boiling point 180° C A current of 3 8 ampères caused vaporisation around the wire   The deflection attained a steady value in about 25 seconds   The scale was straight and the galvanometer faced its middle point.   Table I contains the deflections corresponding to various currents in the heater (for scale distance of 100 cm.), and also deflection/current in each case   The values are plotted in fig. 1 and the resulting direct reading scale is shown in fig 2

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* J. H. Dellinger, 'Bulletin of Bureau of Standards,' vol 10, p 92 (1913).

† In the paper already cited Dellinger describes a bolometric ammeter in which the heated wires are immersed in oil.

‡ The behaviour of a heated wire in a liquid is further illustrated in an Appendix to this paper.
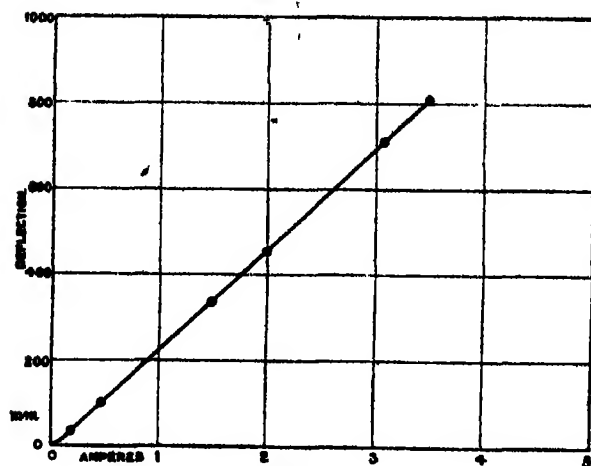
Fig. 1
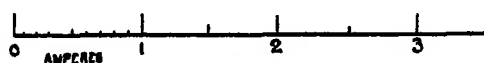
Fig. 2

Table I.

Current, I	Deflection, D	D/I
ampères	mm	
0·20	36·0	180
0·50	104·7	209·4
1·00	221·0	221·0
1·50	336·4	224·3
2·00	450·5	225·2
3·09	710	234·3
3·50	810	231·4

From the Table and those diagrams it will be seen that the scale is uniform over a large range. We have not yet fully investigated the conditions for constancy or temperature coefficient in immersed heater ammeters of this type, but in the experiments described below they proved very useful when frequently calibrated with direct current. In the earlier experiments a thermopile of iron and constantan was used with a straight wire heater. With this combination an interesting effect was observed, it was found that, as the frequency was raised, the same current gave higher and higher readings on the galvanometer, errors of the order of 5 per cent. being noticed at a frequency of 2,000,000 ~ per second. It was found that the errors practically disappeared when the heater wire was bent back in a close narrow loop so as

to reduce as far as possible the magnetic field produced by the current in it
With a single straight heater the magnetic field near it due to a current of
1 or 2 ampères produces considerable magnetisation in the iron of the nearer
thermojunctions, and at the higher frequencies the power dissipated by
hysteresis and eddy currents accounts for the extra heating which caused the
errors. To avoid the possibility of error from this cause (which has much
more effect in the oil-cooled wires, running as they are at high current density),
the iron-constantan thermopiles were mostly replaced by manganin-constantan
ones

While the system of oil-cooled heater gives trustworthy results when used
with care, its range (say, to 10 ampères) is too restricted for the more extreme
practical requirements

The next method, which we now proceed to discuss, consists in the use of
current transformers, and its range of application extends to the largest
currents that can be produced

Current Transformers —Some years ago it was proved by one of us[*] that a
large alternating current could be measured with accuracy by the help of an
air-core transformer in conjunction with a low-reading ammeter. The proper
conditions of working were investigated and the suitability of iron-cored
transformers was also discussed Since that time current transformers have
come into very wide use in the measurement of low frequency currents More
recently Mr T L Eckersley pointed out to us that the above-mentioned
investigation of air-core transformers was perfectly applicable to undamped
alternating currents of high frequency, and he also showed from the theory
that, even where there was considerable damping, good accuracy should be
attainable. At that time he actually used such a transformer in high frequency
experiments[†] We have recently designed a number of current transformers
specially adapted to meet the demands of modern high frequency practice,
before describing these and the tests made upon them, the theory of the
current transformer with damped high frequency currents will be briefly
stated.

Air-core Current Transformer with Damped Alternating Currents.—Let
the secondary circuit of the transformer be connected directly to the
ammeter (heater or other system), this complete circuit having resistance
R_2 and self-inductance L_2. Let the mutual inductance from primary to
secondary circuit be M and the frequency be n, ω being written for $2\pi n$

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[*] A. Campbell, 'Phil. Mag,' Sept., 1896, p. 271.

[†] In the Dönitz wavemeter ('Elektrotechnische Zeitschrift,' vol. 24, pp. 920 and 1024
(1903)) a small variable current is used to connect the resonating circuit to the heater of
the air thermometer, which serves as a current indicator

and j for $\sqrt{-1}$ Following Eccles,[*] when "a long continued slowly damped train of oscillatory current of the form $e^{-bt}\cos\omega t$" passes through the primary circuit (where $b = n$ times the logarithmic decrement per period), we may use the operator $(-b+j\omega)$ in place of the simple operator $j\omega$ used for ordinary continuous alternating currents

If i_1 and i_2 be the instantaneous values of the primary and secondary currents respectively, and I_1, I_2 the corresponding effective values, we have

$$[R_2 + L_2(-b+j\omega)]\, i_2 = -M(-b+j\omega)\, i_1$$

Hence
$$\frac{I_1^2}{I_2^2} = \frac{(R_2-L_2 b)^2 + L_2^2\omega^2}{M^2(b^2+\omega^2)} = \frac{L_2^2\{1+[(R_2-L_2 b)/L_2\omega]^2\}}{M^2(1+b^2\omega^2)}. \tag{1}$$

For such a value of the damping that

$$b = R_2/2L_2 \tag{2}$$

we have
$$I_1/I_2 = L_2/M \tag{2a}$$

If b/ω and $R_2/L_2\omega$ are both small compared with 1, we have

$$\frac{I_1}{I_2} = \frac{L_2}{M}\left(1 + \frac{R_2(R_2-2L_2 b)}{2L_2^2\omega^2}\right). \tag{3}$$

If $R_2/L_2\omega$ is small enough, then I_1/I_2 is very nearly equal to L_2/M, and this value becomes more and more nearly exact as the frequency is raised

When the oscillations are continuous, $b = 0$ and equation (1) takes the well known form

$$\frac{I_1^2}{I_2^2} = \frac{L_2^2}{M^2}\left(1 + \frac{R_2^2}{L_2^2\omega^2}\right) \tag{4}$$

To find in what circumstances the approximation in equation (3) is sufficiently accurate, let us consider what values of b/ω and $R_2/L_2\omega$ are likely to occur in practice. In radiation telegraphy the wave-lengths commonly range from 300 to 6000 metres, the corresponding limits of n being from 6×10^6 to 3×10^5 Since $b/\omega = (\log\text{ decrement})/2\pi$, unless the damping is excessive, b/ω will not be greater than 0·05   It will be found that, by suitable design of the transformer and heater, $R_2/L_2\omega$ can usually be kept smaller than 0 05.   When these two limits are not exceeded, it will be seen that equation (3) is a sufficiently near approximation for practical purposes (within 1 in 1000)   As will be seen from some of the actual transformers described below, the correction term in (3) can generally be made negligible, and the ratio of currents is given by L_2/M.

If on the contrary the damping is excessive, then equations (2) and (2a) afford a possible means of determining b, by altering R_2 until the observed current ratio becomes L_2/M, in which case $b = R_2/2L_2$.

* 'Phys. Soc. Proc.,' vol. 24, p. 260 (1912).

Description of the Air-core Transformers.—Several air-core transformers were constructed with the windings adjusted by measurements at low frequencies (800 ∼ per second) to give exact values of L_s/M, which may be called the "nominal ratio" Ratios of 20 1, 50·1, 100 1 were found convenient. The secondary coil was of highly stranded wire wound in single layer on one (or two) ebonite bobbin (or bobbins), and the primary consisted of one or more turns of thicker stranded wire fastened in fixed position inside the bobbin The final adjustment of the nominal ratio was effected by slightly altering the position of the primary winding The bobbins were of 8 to 15 cm. diameter, and of various lengths, the wire of the secondary circuits having 7 or 17 insulated strands of 0 19 mm. diameter, or, in the latest type, $3 \times 3 \times 3 \times 3$ strands of 0 08 mm diameter. The ends of the primary and secondary coils were brought out to a considerable distance at opposite ends of an ebonite base This was done in order to avoid bringing the leads too near the coils Except in the case of the astatic coils, readings were always repeated with the leads of the primary terminals interchanged; by taking the mean of the two readings the inductive effects of the surrounding circuits were eliminated

Tests on Air-core Transformers—Each transformer was tested at a number of different frequencies from 50,000 to 2,000,000 ∼ per second, the corresponding wave-lengths being from $\lambda = 6000$ to 150 metres. From an oscillating circuit across a spark gap with large magnesium electrodes high frequency current was induced into another tuned circuit containing a self-inductance coil, an adjustable oil condenser, an oil-cooled heater, and the primary coil of the transformer, the secondary being directly connected to another heater (in air) The thermopiles of the two heaters were connected through suitable resistances to reflecting moving coil galvanometers of 10 to 15 ohms resistance. These galvanometers had phosphor bronze (not silver) suspensions; their sensitivities were of the order of 70 mm at 1 metre distance per microampère Heaters of various resistances were used (0 25, 1, 15 ohms, etc.). The sensitivities may be judged from one example : a current of 50 milliampères in a 1-ohm heater gave a deflection of 500 mm. at 1 metre, the movement of the light spot being quite prompt. To ensure the highest accuracy, before and after the high frequency readings the two scales were tested at the same readings by means of direct current. A number of readings of I_1 and I_2 (the respective high frequency currents) were thus obtained, and from their means the ratio I_1/I_2 was deduced. The values of I_1 were of the order of 1 to 2 5 ampères. The steadiness was good, and the individual readings were very consistent among themselves. Table II gives the results obtained with several of the transformers. The

last column but one gives the values of L_2/M from measurements at low frequency (800 $\sim$ per second), the L_2 including the self-inductance of the heater circuit (about 0·4 microhenry)   It will be seen from these results that between very wide limits of frequency (50,000 to 2,000,000 $\sim$ per second) the current ratios are remarkably constant, and with one exception explained below in good agreement with the values of L_2/M determined at low frequencies   As is shown by the last column, the observed variations in ratio are largely accounted for when the more exact formula (3) is taken (b being neglected), and when, instead of determining the L_2 at low frequency, its actual value at the high frequencies is determined by wavemeter observations   It was found that in transformers Nos. 375 and 376 the L_2 fell off by about 1 5 and 2 per cent respectively, when the frequency was raised to about 1,000,000 $\sim$ per second   This diminution was evidently due to the subdivision of the stranding (wires 0 19 mm diameter) not being sufficiently thorough   In transformer No. 411 the secondary coil has very much better stranding, and as a result the ratios are more nearly correct at the higher frequencies   As its L_2 is rather too small (202 8 microhenries) the resistance correction becomes important at $\lambda = 6000$ when a 15-ohm heater is used, but the accuracy is satisfactory when the proper heater of 1 ohm resistance is used in the secondary circuit

Table II —Air-core Transformers.

No	L_2.	Resistance of heater	Wave-length, λ	I_1/I_2 observed.	Low frequency L_2/M	Corrected L_2/M.
	microhenries	ohms	metres			
L 411	202 ·8	17 0	150	99 ·6	100 2	
		17 ·0	300	100 2	100 ·2	100 2
		17 ·0	1500	100 ·3,	100 ·2	100 ·5
		17 ·0	6000	104 ·2	100 ·2	104 ·2
		1 ·0	6000	100 8	100 ·2	100 ·2
L 376	256 4	1 ·0	150	49 ·5	50 ·0	
		1 ·0	300	50 ·3	50 0	50 ·0
		1 ·0	1500	50 ·4	50 ·0	50 ·2
		1 ·0	6000	50 ·5	50 0	50 ·2
L 375	363 ·0	1 ·0	150	19 ·98	20 17	
		1 ·0	300	20 ·06	20 ·17	19 ·99
		1 ·0	1500	20 ·20	20 17	20 24
		1 ·0	6000	20 22	20 ·17	

It should be remarked that, due to the limitations of generating apparatus, the tests have been made with comparatively small values of the primary current.   The properties of air-core transformers depend, however, in no way

upon the absolute values of the currents, as long as the coils have sufficient current carrying capability   The 100:1 transformer had a well stranded primary circuit, capable of carrying 10 to 20 ampères, and the others had proportionate capabilities   Thus a thermal ammeter reading to 0·1 ampère may have its range extended with good accuracy to 10 ampères, and there is not the slighest difficulty in constructing similar transformers to extend the range to 50 or 100 ampères

Possible Sources of Error —To test whether the distributed capacity, which is appreciable in most coils, has any influence upon the current ratio, a condenser of 250 microfarads was put across the terminals of the secondary coil of one of the transformers. As this scarcely affected the readings, it was concluded that, in general, the action of the distributed capacity is negligible The primary and secondary windings, however, should have the relative position of their turns so arranged as to avoid currents due to inter-capacity.*   To prevent the possibility of errors due to proximity to other parts of the circuit, it is desirable to build the air-core transformers with double primary and secondary coils, connected so as to give astaticism in the well known manner

Iron cored Transformers —There is a very general belief that the use of iron in high frequency measuring instruments is almost impossible, since hysteresis and eddy current effects become so pronounced when the magnetic cycle is repeated at such frequent intervals.   In the case of current transformers, however, this is quite a mistake, for, as will be seen below, most excellent results can be obtained by the introduction of iron cores, and it is not even necessary to use specially thin iron sheet or wire in making these.   One or two examples will illustrate this statement .—

Example 1. A number of circular ring stampings from silicon-iron sheet about 0 4 mm thick were placed together (with insulation between them), to form an anchor ring of section about 1 5 sq cm. and mean diameter 4 7 cm. On this ring, well insulated with paraffined silk, was wound very evenly the secondary coil of 200 turns of thin insulated wire   The primary coil consisted of two turns of stranded conductor arranged to pass centrally through the ring and return symmetrically at a fair distance from it, as shown in fig. 3.

After slight adjustment of the relative positions of the primary turns and the ring at a wave-length of 150 metres, the current ratio was tested at various frequencies, and also, for the lowest frequency, with several different values of the primary current I_1 The results are given in Table III.

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* The capacity from primary to secondary was from 20 to 30 micromicrofarads.
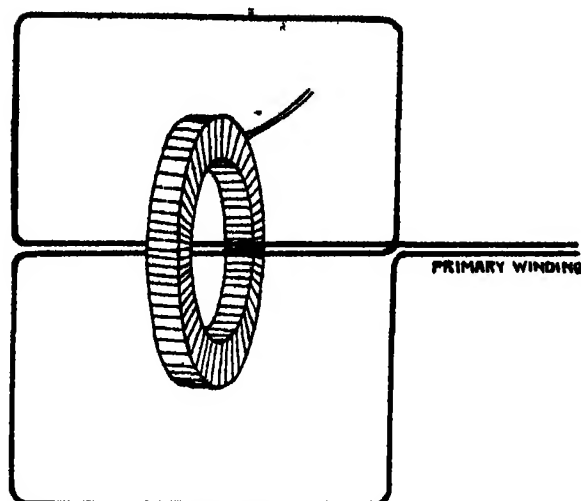
Fig. 3.

Table III —Iron-core Transformer (A)

Resistance of heater	I_1	Wave-length.	Observed ratio, I_1/I_2	Ratio of turns, N_2/N_1
ohms.	amps,	metres		
8 ·0	1 2	150	100 ·15	100 ·0
8 ·0	1 2	300	100 ·6	100 ·0
8 ·0	1 2	1500	100 6	100 ·0
8 ·0	1 2	6000	100 4	100 ·0
8 ·0	2 ·0	6000	100 ·6	100 ·0
8 ·0	6 ·0	6000	100 6	100 0
1 4	6 ·8	6000	100 ·6	100 ·0

From Table III it will be seen that this little transformer, although very simple in construction, gives excellent results, the ratio I_1/I_2 remaining very constant over the very extended range of frequency, and being also very nearly equal to the ratio of the secondary to the primary turns.   Tests at $\lambda = 6000$ showed practically no variation with current.   The last line in the Table refers to a test made with a Duddell portable thermo-ammeter in the secondary circuit, the result is identical with the others, which are for an 8-ohm heater with thermopile and galvanometer

Example 2 · The same core with 200 turns was tested with a single primary turn formed by a stranded conductor passing centrally through the ring and split up and brought back in two symmetrical loops. For wave-lengths of 150, 300, 1500 and 6000 metres the current ratio (I_1/I_2) was found to be 201·0, 200·0, 202·6, and 204·2 respectively. *As might be*

expected, it is not so easy to arrange a single primary turn to give such a good result as with two or more turns The central conductor might with advantage be split up into a considerable number returning back symmetrically in loops If the current to be measured is in a long straight conductor, the iron core with the secondary winding can be slipped over this in the way familiar with low frequencies.

Example 3 · Fair results were also got with a transformer having a core of thin silicon-iron wire (0 125 mm diameter) The primary and secondary turns were 2 and 900 respectively, giving a nominal ratio I_1/I_2 of 450 Approximate measurements gave the following results :—

<div align="center">Table IV</div>

Wave-length.	Variation from nominal ratio
metres	per cent
150	−3 3
300	+3 8
1575	+0 8
6000	−0 4

Measurement of Very Small Currents.—Transformers may be used in measuring small currents to transform a small current up to a larger one, which a given instrument may be capable of measuring. Of course, the effective resistance of the combination is larger than that of the instrument alone in a somewhat greater ratio than the $(I_2/I_1)^2$ In practice it is difficult to avoid also introducing considerable self-inductance, as the secondary winding is not sufficiently short-circuited to annul all the primary effective self-inductance At the higher frequencies this self-inductance may be objectionable If too extreme ratios, however, are not attempted, a properly designed transformer may be very useful, as the following example shows.

Example 3 : A small transformer with iron core similar to that of Example 1 had $N_1 = 200$ and $N_2 = 80$ Working on an 8-ohm heater the ratio I_1/I_2, which should have been 0·400, showed the following variation ·—

<div align="center">Table V.</div>

Wave-length	Variation in I_1/I_2.
metres.	per cent
420	−1 ·0
1500	+4 ·2
6000	+4 ·7

In combination with a Boas vacuum thermojunction of 2·4 ohms resistance, 5 milliampères gave a deflection of 500 mm at 1 metre, the galvanometer circuit having a resistance of 17 ohms

No doubt thinner sheets or wire for the cores would be an improvement, so as to allow the permeability to rise and give a higher value of L_2, which is always desirable

General Conclusions.

It is evident from our experiments that properly designed air-core transformers, when used with due care, in conjunction with thermal ammeters, afford a simple means of measuring currents of the order of 1 to 50 ampères with good accuracy at frequencies from 50,000 up to 2,000,000 ~ per second. Iron cored transformers, which have some advantages in ease of construction, can also be designed to fulfil the same purpose and to give very satisfactory results.   To a limited extent both types are useful for measuring very small high frequency currents

In conclusion, our best thanks are due to Dr R. T. Glazebrook, our Director, for his kind interest and help in the work

APPENDIX.

On the Behaviour of an Immersed Heater.

The behaviour of a thermopile (or more simply a pair of thermojunctions) near a heater wire in oil has already been described for a particular relative position of the heater and junctions.   The general action seems to be that the upward stream of hotter liquid rises more quickly (perhaps widening out) as the heating current is raised ; thus the temperature indicated by the thermojunction is not proportional to the square of the current, but is considerably less.   With various relative positions of heater and junctions very curious curves can be obtained, for example that shown in fig. 4.
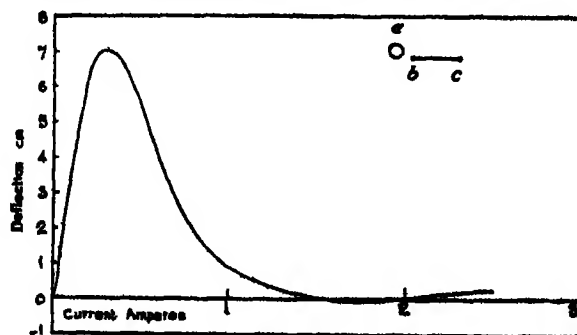
FIG. 4.
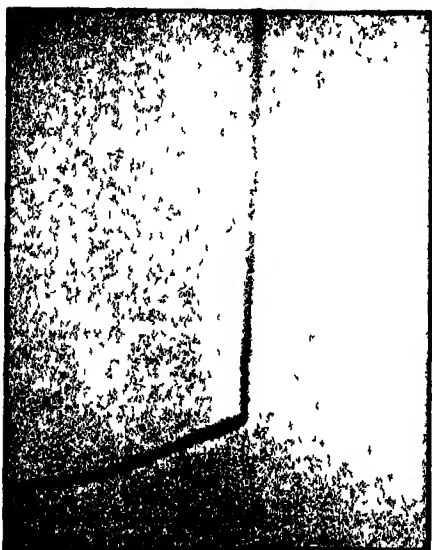
FIG 5.
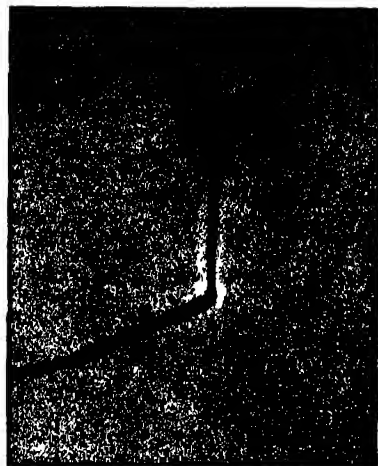
FIG 6.
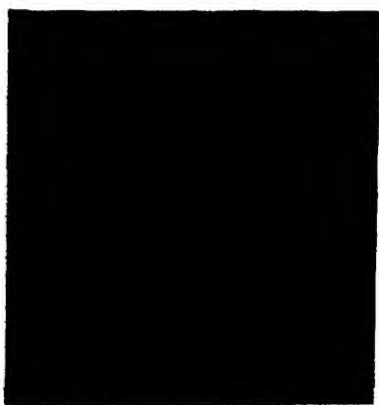
FIG. 7.
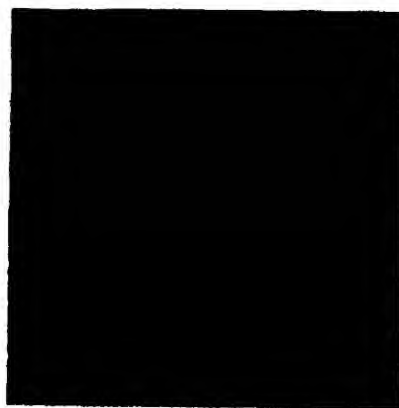
FIG 8.

With the positions as in *a, bc,* the temperature difference first rises and then falls off to zero, becomes slightly negative, and then rises again, as the current is gradually raised

It is very interesting to watch the behaviour of the heated liquid by projection with a strong light. Figs. 5 and 6 (Plate 10) show the stream for currents of 0·5 and 2 ampères respectively, the heater being horizontal and perpendicular to the plane of the picture, and the objective focussing a plane slightly nearer the screen than the heater was   It will be noticed that with the higher currents the hot stream keeps extraordinarily straight and uniform even right up to the surface of the liquid *   In fig 7 is shown the wave set up when the current (2 5 ampères) is switched on

In our earlier experiments we observed a curious effect   after boiling had taken place (even momentarily) when the current had been reduced to a lower value, the galvanometer reading was much too low, but normal conditions were restored if the current was reduced to 0 and then raised to the required value

The experiment recently exhibited by Mr C. W C Crawley and Dr. S W. J. Smith† explains this strange behaviour perfectly, for they show that when the current is reduced from the vaporising value, a little bubble keeps oscillating along the wire, going slower and slower as the current is further lessened, and at last leaving the wire when the current is small enough.   As long as the bubble is on the wire, the agitation it produces in the liquid causes large reduction in the temperature difference indicated by the galvanometer, and accounts for the anomalous readings.   Fig. 8 shows the appearance of the hot stream when the bubble is oscillating along the wire.

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* We may mention that the viscosity of the paraffin oil alters very much with change of temperature, being about 0·025, 0·017, and 0·014 (C.G S units), at 10°, 30°, and 50° C respectively, the corresponding densities being about 0 80, 0·79, and 0 775

† 'Phys. Soc. Proc.,' 1914.

On the Conductivity of Salt Vapours.

By S. J KALANDYK

It has been shown by Beattie,[*] Garrett,[†] and Garrett and Willows,[‡] that when certain salts are heated up to 300–400° C one can observe the discharge of positive and negative electricity This phenomenon is observed more particularly in the case of the halogen salts of cadmium, zinc and ammonium. The researches of Schmidt[§] and Sheard[||] have shown that the discharge is due to two factors, (1) emission of the charges from the surface of the heated salt, and (2) to the conductivity of the salt vapours themselves. The thermionic effect of the above-mentioned salts was studied in detail by Prof O W Richardson[¶] and his pupils, while some investigations of the electrical properties of the salt vapours were made by Schmidt in the papers referred to above The object of the present research was to investigate the influence of the temperature, water vapour, time, etc., on the current passing in the salt vapours.

The Thermionic Effect of the Salt and the Conductivity of the Salt Vapours.

Some experiments were carried out in order to test whether the conductivity of vapours is due to charges which have diffused to other parts of the apparatus from the surface of the heated salt For this purpose the vapours were investigated after passing through a cylindrical condenser in which the electric force was strong enough to sweep all charged particles to the electrodes The apparatus used consisted of a small bulb A (fig. 1), in which the cadmium iodide was placed. The vapour at first passed through the plug of glass wool B to stop the large ions which might be produced during the heating of salt, then entered the condenser K_1, where the smaller ions could be removed by the electric field. The outer coating of the condenser K_1 was obtained by platinising the inner surface of the glass tube with a "liquid platinum" (from Deutsche Gold und Silber Scheide Anstalt) and was connected to earth. As the inner coating of the

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* Beattie, 'Phil. Mag.,' vol 48, p 97 (1899).

† Garrett, 'Phil. Mag.,' (6), vol. 13, p. 728 (1907)

‡ Garrett and Willows, 'Phil. Mag.,' (6), vol. 8, p. 437 (1904).

§ Schmidt, 'Ann. d. Physik,' (4), vol. 35, p. 401 (1911), and (4), vol. 41, p. 873 (1913).

|| Sheard, 'Phil. Mag.,' (6), vol. 25, p. 370 (1913).

¶ O. W Richardson, 'Phil. Mag.,' (6), vol. 26, p. 452 (1913).

condenser a glass rod covered with the same substance was used, and was connected by a platinum wire with the source of electromotive force.

For measuring the ionisation of the vapours a second cylindrical condenser K_2 was used. It consisted of an outer earthed platinum tube about 10 cm. long, in the axis of which a short platinum tube was fixed, the latter being connected to a gold leaf electroscope Preliminary experiments were first made in order to test the action of the condenser K_1 For this purpose the bulb A was replaced by an open tube in which was placed a fine platinum strip which could be heated by an electric current The tube D was connected with a water pump, and thus a stream of air was obtained which carried the ions emitted by the hot platinum upwards. When the electroscope was charged up to $+200$ volts, and both coatings of the condenser K_1 were earthed, it was found that the potential of the leaf fell 2 volts in five seconds. It required, however, about 90 seconds to fall the same amount when the inner surface of the condenser K_1 was charged up to ± 200 volts. It follows, therefore, that by this arrangement it is possible to stop practically all the ions entering the condenser K_1

To test if the ionisation observed in the salt vapours is due to the surface effect, the bulb A was filled with 5 grm. of cadmium iodide, the whole apparatus was exhausted by cooled charcoal to the pressure 10^{-3} mm of mercury and heated in the electric furnace to $298°$ C When the current in the upper condenser became constant the inner surface of the condenser K_1 was charged up to 200 volts as in the previous experiment, and the current in the condenser K_2 was measured during about 15 minutes The difference between the readings with and without K_1 charged did not exceed the error of the experiment. Therefore we may conclude that the ionisation observed in the vapours is mostly due to the process which is going on in the vapours themselves, and is practically independent of the emission of charges from the surface of the heated salt. It may be remarked that Sheard (*loc. cit.*), working with apparatus of different construction, came to the same conclusion.
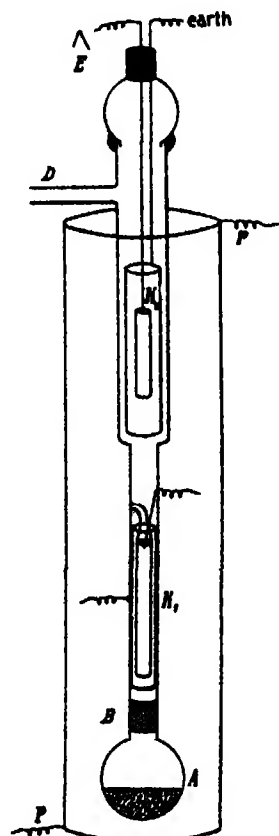
Fig 1.

Influence of Water Vapour.

The influence of water on the conductivity of salt vapours has been studied by various experimenters, but the question is not yet definitely settled. Garrett, in the paper referred to above, noticed that when carefully dried zinc iodide was heated, no leak was observed; he therefore came to the conclusion that, in the case of this salt, water vapour is necessary for the production of ionisation. Quite recently Dr Willows* again called attention to this point Schmidt (*loc cit.*), however, observed no difference between the conductivity of salt vapours in dry air and in the air which had been passed over boiling water

To decide this important question the influence of water on the conductivity of salt vapours was studied in the following apparatus (fig. 2) The vapours
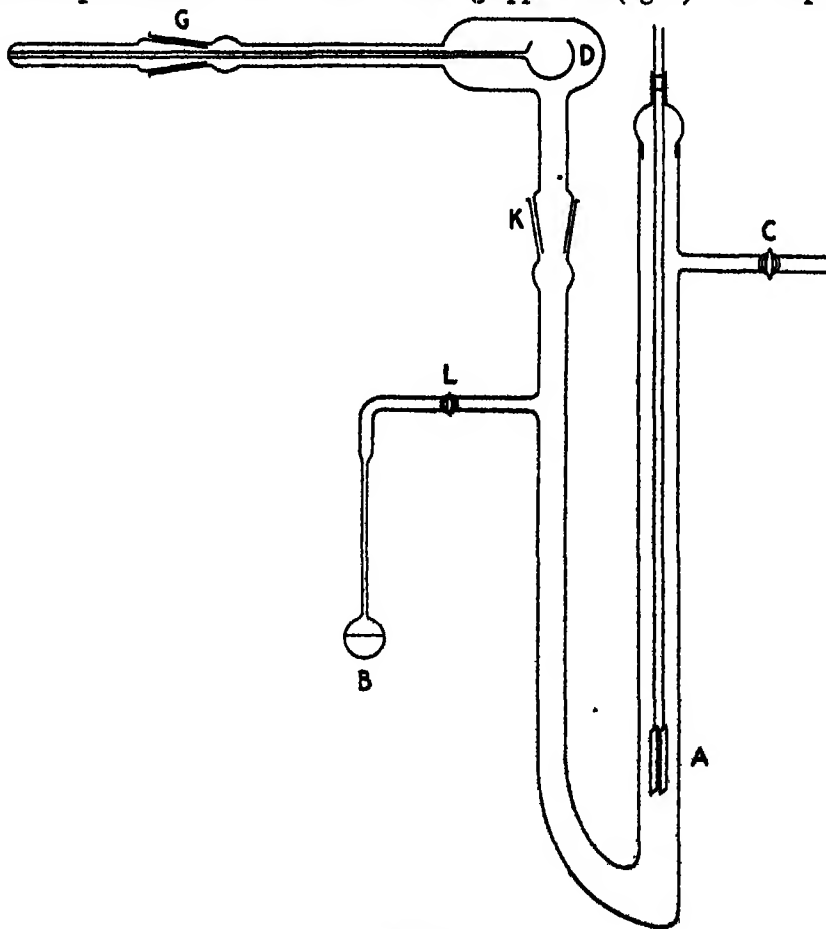
FIG. 2.

* Willows, 'Phil. Mag.,' (6), vol. 24, p. 691 (1912).

were investigated in the tube A (12 mm. diameter), which was connected through the tap C with a manometer, pump and charcoal tube   The salt was placed at the bottom of the tube and at a distance of 4 cm two platinum plates were fixed (1 5 sq. cm. surface, distance between the plates $= 0\cdot5$ cm.). One of the plates was connected to a Wilson electroscope (12·5 divisions per ' volt) and the second kept at the potential -200 volts   Preliminary experiments showed that, for the same potential difference, the current obtained was much smaller when the potential was applied for a long time than in the case when the electrode was charged only during the measurements   Therefore, to keep the conditions steady, the plate was always connected with one pole of the storage cells.   The water was placed in a small bulb B separated from the main apparatus by the tap L.   (The upper part K was not used in this experiment)   The lower end of the apparatus was placed in the electric furnace.   To free the bulb of air the water was frozen with liquid air and the whole apparatus exhausted with charcoal.   The stopcock L was then turned on and the ice allowed to melt.

At first an experiment was made in order to test whether the presence of the water vapour had any action on the insulation.   For that purpose the empty apparatus was exhausted and heated up to about $280°$ C, then the stopcock C was closed and L opened   The observations showed that after about 15 minutes a small conductivity over the surface of the insulation appeared, but in any case this current was negligibly small in comparison with that which was obtained when the tube was filled with salt vapour

The influence of water was tested for the salts cadmium iodide, zinc bromide, zinc iodide, potassium chloride, and potassium iodide, and the results obtained are set out in Table I, p 638.

In the case of cadmium iodide 1 grm was used and the apparatus exhausted to 10^{-4} mm. of mercury and heated up to $264°$ C.   In the case of zinc bromide 1 grm. of the salt was placed in apparatus and kept one day in charcoal vacuum to liberate all water vapour, which is known to be very easily absorbed by this substance.   The pressure was 16.10^{-2} mm. and the temperature $295°$ C.

For zinc iodide 0·3 grm. was dried four days in a charcoal vacuum.   The temperature was $270°$ C., and the pressure at the beginning of the observations was 3.10^{-5} mm.   All the salts were obtained from Kahlbaum.

As may be seen from the Table I water vapour has a very marked influence on the current passing in the salt vapours.   The greatest increase of the conductivity was observed in the case of zinc iodide, which is also the most hygroscopic substance of those investigated.   The curious point is that the greatest conductivity is observed when the reservoir with the water is cut

Table I.

Cadmium iodide.		Zinc bromide		Zinc iodide	
Time	*Current	Time	Current.	Time.	Current
min		min		min	min
0	19·8	0	64·5	0	24 1
6 8	19·4	3	52 6	11	22·7
7 3	L opened	L opened, C closed		L and C opened	
	C closed	4 7	182	13	60 6
9 3	29 0	9	250	L opened, C closed	
13 3	38 1	L closed, C opened		19	200
16	43·5	11	333	22	213
16 5	L closed	13	200	L closed, C opened	
	C opened	17	182	24 5 ·	286
19·8	37 7	21 5	143	28 8	400
25 3	30 3	Again L opened		48 6	32·3
31 8	30 3	C closed		Again L opened	
		30·5	167	C closed	
		33	200	56 5	105
		35	222	L closed, C opened	
		L closed, C opened		67	62·5
		39·2	250		
		43	117		

* Arbitrary units.

off and the water vapour begins to get absorbed by the charcoal and phosphorus pentoxide This phenomenon may be due to the fact that the conductivity of the salt vapours depends not only on the presence of the water, but also on the pressure of the gas filling the apparatus It was shown by Schmidt that increase of pressure diminishes the current It may therefore be expected that the rapid absorption of water vapour will be accompanied by an increase of the current

Of the salts which do not show any conductivity when heated, potassium chloride and potassium iodide were tested. It was especially interesting to test the influence of water vapour on the last substance, as H. A. Wilson[*] observed a large current when a solution of KI was sprayed into a hot platinum tube (270° C.). Garrett, however, noticed no leak when the dry salt was heated to the same temperature. The experiments with this substance were carried out with a somewhat different arrangement. The Wilson electroscope was replaced by a quadrant electrometer giving 50 divisions per volt. The water vapour was absorbed by a tube immersed in solid carbon dioxide, and for measuring the current a small cylindrical condenser was used instead of the two platinum plates; 3 grm. of KI were placed in the tube A and heated for two hours at a temperature of 308° C. The apparatus was exhausted with a Gaede pump to 10^{-4} mm.

* H. A. Wilson, 'Phil. Trans.,' A, vol. 197, p. 415 (1901).

The outer tube of the condenser was charged to +100 volts, and the inner was connected with the electrometer At the commencement of heating a small leak was observed, which did not persist long, however, and the electrometer became perfectly steady When the stopcocks L and C were opened and a stream of water vapour was admitted into the tube A a considerable deflection was noticed (five divisions in 10 seconds). When the stopcock L was closed the current disappeared also. The phenomenon was repeated several times with identical results.

Potassium chloride was tested in the previous arrangement (with the Wilson electroscope); when the dry salt was heated to the temperature 303° C at a pressure about 10^{-4} mm. no current was observed as in the case of KI In the first moment when the water vapour was admitted the gold leaf showed a small and irregular movement, this current, however, diminished gradually, and in a few minutes the water did not produce any leak Very likely the initial increase was also due to some secondary effect.

Change of Conductivity with the Time.

This question has been the subject of many investigations Garrett has shown that the conductivity produced by heated salts increases for about 20 minutes up to a certain maximum and then begins to fall The relation between the current and the time was found to be expressed by the formula

$$i = A\,(e^{-\lambda_2 t} - e^{-\lambda_1 t}),$$

where A, λ_1, and λ_2 are constants. In his last paper Schmidt suggested the idea that the decrease of conductivity is due to two factors (1) to the diminution of the surface of the salt during the heating, and (2) the change of concentration of ions due to their removal by the electric field

The experiments described in the previous paragraph show that the water vapour has enormous influence on the current passing in the salt vapours. It was interesting, therefore, to test if the initial stage of conductivity is not also complicated by water vapour, which is usually absorbed by the salts and liberated during the heating. For that purpose some measurements were made in conditions when all possible care was taken to get rid of traces of water vapour present in the apparatus Cadmium iodide was used for this, as it does not contain any water of crystallisation, and therefore one can remove the water vapour absorbed by the salt by careful drying *in vacuo*. The apparatus described in the previous paragraph was used for the measurements. To have a supply of the dry air the bulb B was replaced by a larger reservoir, in which the air could be kept in presence of phosphorus pentoxide. To follow in more detail the initial stage of

conductivity, the salt was not heated together with the tube A, but it was placed in a small glass spoon D, whence it could be thrown into the apparatus by turning the ground glass connection G Two sets of measurements were made with cadmium iodide—

1. The salt was placed into the spoon D, the apparatus was exhausted to 0 75 mm and immediately heated

2 The apparatus with cadmium iodide in the spoon D was exhausted with charcoal to about 10^{-3} mm. and kept at that pressure for about five hours. The apparatus was then filled with air which had remained a few days in contact with phosphorus pentoxide. By opening the charcoal tube the pressure was then reduced to 0·51 mm.   The readings obtained in both cases are given in Table II and in the diagram, fig 3

Table II.

Not dried; temperature = 271° C.			Dried; temperature = 285° C.		
Time.	Current	Pressure.	Time	Current	Pressure
min			min.		
0 0	Salt thrown down	0 ·74	0 ·0	Salt thrown down	0 ·51
3 1	4 5	0 9	5 5	1 25	Constant
7 2 ,	6 ·7	—	10 ·0	4 2	
9 5	—	0 ·82	16 ·7	7 1	
12 5	31 ·0	0 ·79	28 ·0	6 ·7	
21 3	50 ·0	0 ·765	36 ·0	7 ·0	
28 ·0	40 ·0	0 ·76	42 ·0	6 ·7	
39 5	29 ·0	0 75	50 ·0	6 ·7	
47 ·0	24 ·0	—	58 ·0	6 ·7	
65 ·0	20 ·0	0 ·75			
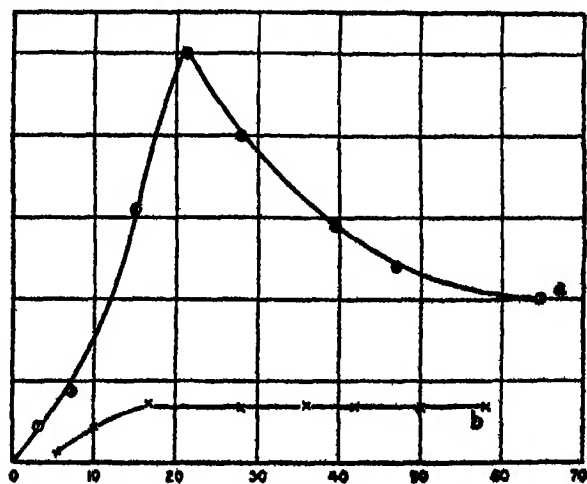
Fig. 3

The curve obtained in the first case (fig 3, *a*) does not differ from those obtained by the previous investigators if we take into account that the initial increase is due to the heating of the salt and to the diffusion of the vapours to the upper parts of the tube On the contrary, the current obtained with dry salt and dry air is practically constant. It is interesting to note that, although cadmium iodide is not supposed to be very hygroscopic, nevertheless it liberates during the heating a considerable amount of water vapour, as will be seen from the change of pressure during the experiment. In a few minutes after throwing the salt into the tube A the pressure increased from 0 74 to 0·9. After that it began to decrease, and after about half-an-hour reached its initial value.

Further experiments with cadmium iodide were carried out in a high vacuum obtained by the cooled charcoal method It was expected that when the salt remained for a longer time in a very high vacuum and the gases liberated during the heating were instantly removed, the current passing through the salt vapours would be more constant For this experiment 1 grm of cadmium iodide was kept for one day in the highest vacuum obtained by charcoal, the apparatus was then heated and the salt thrown down The readings obtained are shown in Table III and fig 4.

During the last experiment the charcoal tube was open all the time and

Table III.

Time	Temperature	Current
min	°	
7·0	267·0	25
12 5	267·0	31
19 3	267 5	46
29·0	268·0	52
89·5	268·0	52
50·5	269·0	55
65 5	268·0	50
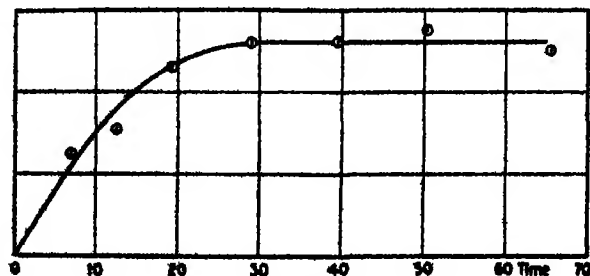
Fig 4.

the pressure of air remaining in the apparatus was about 3×10^{-5} mm. The electrode was charged the whole time to -200 volts. The furnace was heated by the main battery of the laboratory and it was difficult to keep the temperature of the apparatus more constant. We may therefore regard the currents obtained after 20 minutes' heating as practically constant.

Thus in the case of cadmium iodide it seems possible to obtain a fairly steady current in the vapours when the salt is properly dried   Similar experiments were made with zinc iodide and zinc bromide, but the influence of drying was not expressed so distinctly as in the previous case.   It may be that such a definite result could be obtained with cadmium iodide because this salt is not very easily volatilised and the change of conductivity due to the diminution of the surface of salt does not play a very great *rôle*.

Influence of Temperature.

The influence of change of temperature on the conductivity produced by heated salts was tested by Garrett and by Schmidt.   In Garrett's experiments the salt was placed on one of the plates of the condenser and heated by an electric furnace surrounding the whole   Thus, the current passing between the plates was due to the emission of the charges from the surface of the hot salt and to the conductivity of vapours.   The component of the current due to the conductivity of vapours was complicated by the change of pressure of the salt vapours   Garrett observed that the current varied with the temperature according to Richardson's law, and it therefore appears probable that in these conditions the thermionic effect of the salt plays the chief *rôle*.   Further measurements of the temperature effect were made by Schmidt, who observed that the conductivity increases with temperature, at first slowly and then more rapidly.   Schmidt's arrangement allowed the conductivity of the vapours to be measured.   However, in his experiments also the constancy of the pressure was not taken into account and therefore the rapid increase of the current might have been due to the change of density of the vapours.

The following set of measurements was made in the conditions where the temperature of the vapours could be varied independently of the temperature of the salt.

Two grammes of cadmium iodide were placed on the bottom of a glass tube (about 1·7 cm diameter) and heated in the electrical furnace to 209° C.   At the distance of about 20 cm. a cylindrical condenser was placed, consisting of a platinum tube 10 cm. long and 2 cm. in diameter, in the centre of which was fixed a narrow platinum tube 2 cm. long and 2 mm. in diameter.   The outer electrode was charged to -200 volts and the inner one connected to a Wilson electroscope   The upper part of the tube was surrounded by a second

electrical furnace in such a way that the vapour passed a distance of about 15 cm. in it before reaching the condenser so as to acquire the temperature of the second furnace. The whole apparatus was exhausted and the salt was kept for one day in a charcoal vacuum. During the experiment the pressure was 6×10^{-5} mm In Table IV the measurements of the current at the various temperatures are given. It was found that the logarithms of the current are in a linear relation with the reciprocals of the absolute temperatures of the vapours (see fig 5, A). Therefore the connection between the current ι and the absolute temperature ϑ may be expressed in the following form

$$\iota = ae^{-\iota/\vartheta}, \tag{1}$$

where a and b are constants. In the top column of Table IV the absolute temperatures calculated according to the formula

$$\iota = 10^{21\cdot3}e^{-2\cdot35 \times 10^4/\vartheta}$$

are given The agreement with experiment is fairly satisfactory.

Table IV

Absolute temperature of vapours— Calculated Observed	467 486	502 499	511 511	522 523	532 533	550 548	562 5 560
Current in arbitrary units	2 78	10 5	21 5	54 ·6	139	575	1450

To follow the connection between the current and the temperature over longer intervals some modifications were made in the previous arrangement The tube containing the salt was made of fused quartz (diameter 1 cm) placed horizontally and joined to the apparatus by sealing wax cooled by a copper jacket. For measuring the temperature of the furnace an iron-constantan thermo-couple was used. It was mentioned above that the electrodes placed in the vapours were connected continuously with the source of potential to secure greater constancy of readings. As the increase of temperature produces a new concentration of ions it was necessary after obtaining the steady temperature to wait a certain time until the equilibrium was reached. As this process goes fairly slowly it was not possible to take readings at many temperatures, otherwise the conditions would not be identical The results obtained in this arrangement with ZnI_2, $ZnBr_2$, and CdI_2 are to be seen in the Table V or on the diagram, fig 5.

The discrepancy between the calculated and observed temperatures is somewhat greater in this case than in the previous one. This disagreement may be due to the variation of pressure of the salt vapours during the experiment,

Table V

Zinc iodide Temperature of salt, 267° C.			Zinc bromide Temperature of salt, 271° C			Cadmium' iodide Temperature of salt, 256° C		
Current	Absolute temperature		Current.	Absolute temperature		Current.	Absolute temperature	
	Observed	Calcu-lated		Observed.	Calcu-lated		Observed	Calcu-lated
7·4	545	541	1·0	570	578	1·4	545	555
83 8	568	591	10·0	635	627	2·68	568	573
625·0	633	638	62·5	663	671	16·7	629	631
2778 0	684	679	2270·0	766	777	55·6	689	677
50000·0	784	777				556·0	761	784
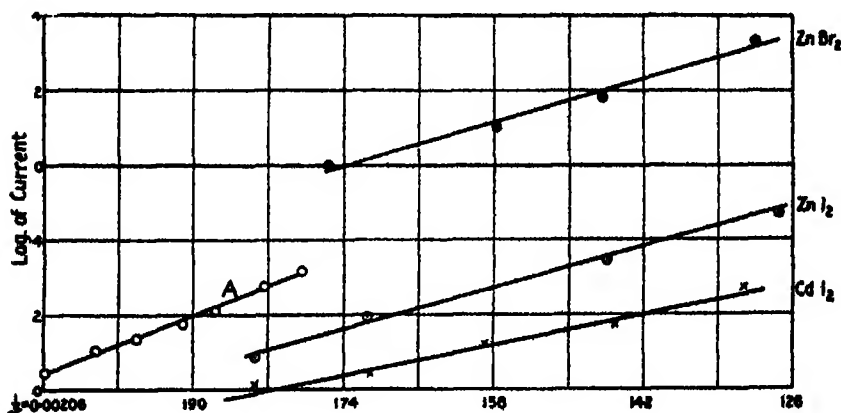
Fig. 5.

which takes a considerable length of time (about 8 hours). Anyhow the linear connection between $\log i$ and $1/\vartheta$ may be accepted as a first approximation. The following formulæ were used for calculation of absolute temperatures in the above Table :—

$$ZnI_2 : \iota = 10^{13\cdot47}e^{-1\cdot57\times10^4/\vartheta}, \qquad ZnBr \cdot \iota = 10^{13\cdot05}e^{-1\cdot74\times10^4/\vartheta} ;$$

$$CdI_2 : i = 10^{9\cdot05}e^{-1\cdot14\times10^4/\vartheta}.$$

In the previous experiments it was shown that the conductivity in the salt vapours is mostly due to the processes which are going on in the vapours themselves. The question now arises whether the observed conductivity is due to the volume ionisation of the vapours or to the chemical action of vapours on the platinum electrodes. An attempt was made to decide this point. The tube, with a sample of cadmium iodide, was

placed horizontally, and the current passing between the plates was measured. One of the electrodes was then removed and covered with spongy platinum powder, so that its surface was greatly increased, while the volume of the vapour between the plates remained practically constant. Therefore, if the observed ionisation was due to the surface effect, it might have been expected that the current would be much stronger than in the previous case. However, the results showed that the current obtained with the spongy platinum electrode was of the same order as in the previous case, consequently this experiment seems to show that the conductivity is chiefly due to the volume ionisation.

If we assume that the conductivity of vapours is due to their electrical dissociation, we may easily calculate the work required to ionise one molecule of vapour, applying the formula of van't Hoff[*]

$$\frac{q}{2}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \log\frac{x_1^2}{x_2^2}\cdot\frac{T_2}{T_1},$$

where q is number of calories required to dissociate one gramme-molecular weight of vapours, x_1 and x_2 are ratios between the number of dissociated and neutral molecules at the temperatures T_1 and T_2. Calculating in this way the energy required to ionise one gramme-molecular weight of vapours and dividing it by the number of coulombs required to electrolyse one gramme-equivalent weight of any substance, we obtain the following values for the ionising potential of different salt vapours :—

	q	w (volts)
Cadmium iodide	$4\cdot4\times10^4$	1·93
Zinc iodide	$6\cdot2\times10^4$	2·72
Zinc bromide	$6\cdot8\times10^4$	2·97

These values are much less than the corresponding potentials for gases

Ionisation and Dissociation

It is known that the salt vapours studied in the foregoing experiments are easily decomposed. It seemed interesting, therefore, to test other substances the vapours of which are dissociated at high temperatures. For that purpose phosphorus pentabromide and sulphur dichloride were tried. The first compound is dissociated at 100° C and the second at 64° C. The experiments were carried out in two different arrangements The first apparatus consisted of a small tube with two platinum electrodes, one of which was charged to 100 volts, and the second connected with a quadrant electrometer. A small bead of phosphorus pentabromide was placed inside

[*] H. A. Wilson, 'Phil. Trans.,' A, vol. 197, p. 415 (1901).

the tube, which was then exhausted with a Gaede pump and sealed off. The tube was placed in an oven, which could be heated with a Bunsen
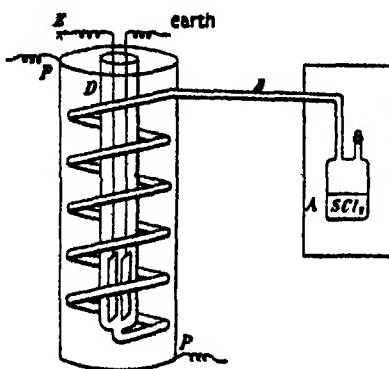
Fig 6

burner In the second arrangement the substance was placed in the small vessel A (fig 6), which was placed in an oven, the temperature of which could be regulated The vapours emerged through the tube B, passed through the spiral, and came into the tube D, in which were placed two electrodes, one of them earthed, and the second connected with the electroscope, charged to about 300 volts. The spiral and the tube D were placed in the electric furnace, so that the temperature of the vapour could be varied without changing the temperature of the substance itself

The experiments carried out with both arrangements have shown that the vapours of the above-mentioned substances do not conduct the electric current when they are dissociated by heat This negative result shows that the dissociation cannot be regarded as the cause of the ionisation

Summary *

The experiments described show—

1 The conductivity of the salt vapours is due to the processes occurring in the vapours themselves.

2 The vapours of carefully dried salts conduct the electric current. Therefore the conductivity cannot be ascribed to the chemical action of water vapour on the salt vapours However, the presence of water vapour increases the current passing in salt vapours.

3 When cadmium iodide was very carefully dried, it was possible to observe a current which was practically independent of time

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4 The connection between the current $\imath$ and the temperature ϑ may be expressed with considerable accuracy by the formula

$$\imath = ae^{-b/\vartheta},$$

where a and b are constants

5 The ionising potential calculated from the energy of dissociation is considerably less than that for the ordinary gases.

6 The dissociation of vapours is not always accompanied by ionisation

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OBITUARY NOTICES

OF

FELLOWS DECEASED.

CONTENTS.

ALEXANDER BUCHAN,* 1829–1907.

ALEXANDER BUCHAN, meteorologist, was born at Kinnesswood, Kinrossshire, on April 11, 1829   Of his early days his son, Dr Hill Buchan, writes —

"His father, Alexander Buchan, died within a day of my father's birth He was engaged in the weaving trade.   His mother's maiden name was Margaret Day Hill   She lived to old age   They had four children, of whom my father was the youngest, two boys and two girls, who survived to a good age, but predeceased my father   The sisters lived at home at Kinnesswood

"His brother's daughter, Jessie Hill Buchan, was for many years, until her death in 1905, the greatly esteemed assistant of her uncle

"Shortly after the father's death, the family removed to the neighbouring village of Milnathort, and remained there for some years, but afterwards— during at least part of my father's boyhood—returned to Kinnesswood

"Kinnesswood was then a small village whose sole industry was hand-loom weaving, but the standard of education and intelligence among the people was very remarkable   I have seen old note books kept by some of the villagers in beautiful penmanship, which showed that they both read and thought, Michael Bruce, the poet, author of 'The Cuckoo' (so often seen in old collections), was born and bred in the village   I have often heard my father say that some of the ablest men he had ever met were among this class there. My father attended a local school in Milnathort, I think, but I am not certain on this point   This education was supplemented by private tuition in Latin, which he got from his minister, Rev   Dr   Laird, to whom for his kindness in this matter my father always felt himself to be under a lasting debt.

"When he went to Edinburgh he entered the Free Church Normal College, which met in Moray House—of many historical associations—in the Canon-gate   This was not a school in the ordinary sense of the term, but a non-residential college for the training of the teachers for Free Church Day Schools in Scotland (at that period the Free Church had separate schools). The education given at Moray House was very good.   I do not know the exact dates of his attendance at Moray House, nor when he entered the University. The two courses were sometimes (in part at least) taken at one time   I think his University course may have been taken in two parts, but, again, I am uncertain.

"He took the ordinary old regulation Master of Arts course at Edinburgh University—Latin, Greek, Mathematics, Physics, Logic and Metaphysics, Moral Philosophy, and English Literature   He took prizes in the classes of Logic and Metaphysics under Campbell Fraser, Moral Philosophy under Macdougall, Mathematics under Kelland, and Physics under Tait.   Though

* This notice is based largely upon "Contributions towards a Memorial Notice of Alexander Buchan, M A., LL.D., F R.S.," 'Journal of the Scottish Meteorological Society,' 3rd series, 1907, vol. 14, No 24.

not actually a student in the Philosophy class when Sir William Hamilton held the chair, he frequently went to hear him, and was very much impressed by Hamilton

"He also took out the Botany class, which was not in the Arts curriculum, under the late Professor Balfour, who became a life-long friend   In August, 1858, he accompanied Balfour and some of his more enthusiastic students on a walking tour through Switzerland, the chief object being to botanise the district round Zermatt.   Mr (afterwards) Sir Joseph Fayrer was one of the company   This was my father's first introduction to the Continent, and left lasting impressions.

"He collected a large herbarium in Scotland and Switzerland   Botany, especially field botany, had great attractions for him as a life work; but the vacancy in the Scottish Meteorological Society turned his life in another direction.   His interest in field botany continued through life.   He never seemed to have any difficulty in naming any plant he saw   This knowledge extended to grasses, mosses, and seaweeds, of which he made collections.

"He held teaching appointments in schools in Blackford, Banchory, and Dunblane (not Dunkeld, as appeared in many papers)   At these places he extended his knowledge of botany and had also time for general reading. At Dunblane he was Keeper of the Leighton Library, which comprised Archbishop Leighton's original collection as well as modern books.   My father was very fond of teaching, and it was a great regret to him to have to relinquish it on account of throat weakness."

At Christmas, 1860, he left school work to take up the appointment of Secretary of the Scottish Meteorological Society, which had been founded in 1855 through the instrumentality of Dr James Stark, head of the Statistical Department of the Office of the Scottish Registrar-General.   In 1887, he was appointed by the Royal Society of London a member of the Meteorological Council, which, from 1877 to 1905, administered the Parliamentary Grant for Meteorology and directed the operations of the Meteorological Office

From the time of his appointment by the Scottish Society Buchan devoted his life to the work of his office and to meteorological research or discussion, in the congenial society of Sir Arthur Mitchell, David Milne-Holme, the Marquis of Tweeddale, Thomas Stevenson, Sir John Murray, and other distinguished Fellows of the Royal Society of Edinburgh, of which he became a prominent figure as Librarian and Curator of the Museum from 1878 to 1906, and Vice-President.   He was Secretary of the Royal Society Club, the social rendezvous of the Society, from 1883 till his death   His tall figure, long thin Scottish face, straight, dark, rather lank hair and long beard, were associated with a suggestion of humour about the eyes that made for sociability and good company   "He worked for the love of work."   He was, above all, tenacious and resourceful.   A close friend of Robert Louis Stevenson, his colleague Thomas Stevenson's son, he had a profound appreciation for and knowledge of literature,

particularly old English poets, dramatists, and historians. He was an office bearer in the Free Church. "His deeply pious nature, his entire freedom from cant of every kind, his liberality of thought, his clear outlook on all subjects, always gave the impression . . of a good man."

He married in 1864 Sarah, daughter of David Ritchie of Musselburgh, who died on May 13, 1900, leaving a son A. Hill Buchan, who took up the profession of medicine and was his father's companion on many journeys for the inspection of meteorological stations. Buchan died on May 13, 1907, at 2, Dean Terrace, Edinburgh, whither he had removed some years previously in order to share a house with his son in a position convenient for medical practice. He was buried at the Warriston Cemetery.

In his scientific work Buchan was naturally the mainstay of the Scottish Meteorological Society and was the chief contributor to its journal, sixty-six of its published papers are from his pen. The work of the Society included not only the holding of meetings and the discussion and publication of scientific papers but also the collection of data, and consequently the organisation and superintendence of a network of stations with a view to the compilation of a body of meteorological statistics. The immediate object of this organisation was the regular supply of information to the Registrar-General of Births, Deaths, and Marriages, for Scotland for whom particulars of all the meteorological elements were required. To these were added the weather journals of the Lighthouses of the Board of Northern Lights, of which Buchan's friend Thomas Stevenson, the designer of the thermometer screen now generally adopted, was engineer, and a separate series of rainfall stations was organised to do for Scotland what G. J. Symons attempted, with conspicuous success, for the British Isles. Except the lighthouses the Scottish stations were maintained by voluntary observers, generally the noblemen and country gentlemen, for whom Buchan's periodical visits of inspection formed a connection with the Society.

The papers published by the Society were often preliminary to more complete discussions published by the Royal Society of Edinburgh or to publication in book form. His best known books are as follows :—

(1) 'The Handy Book of Meteorology,' first published in 1867, second edition 1868 (Blackwood and Sons), which has become a recognised text-book of meteorology all over the world.

(2) 'Introductory Text-book of Meteorology.'

(3) "Report on Atmospheric Circulation, based on Observations made on board H.M.S. *Challenger* and other Meteorological Observations," 'Reports of the Expedition of H.M.S. *Challenger*, Physics and Chemistry,' vol. 2, part 5, 1889 (H.M. Stationery Office).

(4) "Oceanic Circulation." '*Challenger* Reports. Summary of Results,' 1895.

(5) 'Bartholomew's Physical Atlas,' vol. 3, Meteorology (with Dr. A. J. Herbertson), 1899.

Buchan's chief work, 'The Atmospheric Circulation,' is the final form of

the discussion of observations of pressure and temperature collected from all parts of the world   Of its precursor, the work on mean pressure, published in the 'Transactions of the Royal Society of Edinburgh,' 1869, von Hann says   "It is even more important than the celebrated work of Dove, 'The Distribution of Heat over the Surface of the Earth,' Berlin (1852)."   It is the document which justifies what Buchan wrote in his preface to the second edition of 'The Handy Book of Meteorology'   "Now that meteorology has discarded all pretensions and theories, except in so far as the latter are the legitimate result of observation, it has acquired rapid development and established its claim to be regarded as the youngest of the sciences.

"The *Challenger* volume extends to 347 pages of text, including tables giving the mean diurnal variation of atmospheric pressure, the mean monthly and annual height of the barometer, the prevailing winds for each month and for the year, as well as tables showing from the *Challenger* observations the deviations each two hours from the mean daily temperature of the surface of the sea, from the mean daily temperature of the air, and from the mean daily atmospheric pressure, and a table for reducing observations of the barometer to sea-level   This report is illustrated by a series of fifty-two coloured maps, showing the mean temperature, isobaric lines, and prevailing winds over the globe for each month of the year and for the year, and by two plates of curves showing deviations at different hours of the day from the mean daily temperature, mean daily atmospheric pressure, wind velocity, etc

"Dr. Buchan's 'Report on Oceanic Circulation, based on Observations made on board H.M.S *Challenger* and Other Observations,' appeared in 1895, and extends to thirty-eight pages of text, illustrated by sixteen coloured maps, showing the mean annual specific gravity and the mean annual temperature at the surface, as well as the temperature at various depths beneath the surface and at the bottom of the ocean.   His paper on 'Specific Gravities and Oceanic Circulation,' published in the 'Transactions of the Royal Society of Edinburgh,' 1896, runs to twenty-six pages of text, illustrated by nine maps, showing the specific gravities observed at the surface and at various depths beneath the surface of the ocean."

Every part of climatology is touched upon in the papers contributed to the Society, and every part of meteorology representable by maps is represented in Bartholomew's Atlas.   Dr von Hann in his memorial notice calls special attention to Buchan's numerous discussions of the relations between the distribution of atmospheric pressure and long-continued weather anomalies as "breaking new ground for a sound advance of meteorology in Central Europe."

Another group of papers which deserves special mention is that which includes the two papers upon the influence of weather on mortality from different diseases and at different ages, and those on influenza and weather in London, all of which were written in conjunction with Sir Arthur Mitchell, and which display a singular felicity in the grouping of statistics

to elicit unsuspected relationships between phenomena which are indirectly connected.

A celebrated enterprise for which the Scottish Meteorological Society was responsible under Buchan's direction was the observatory at the summit of Ben Nevis, the highest point of the British Isles, 4406 feet above the sea-level, for which permanent buildings were finished in November, 1883, after some preliminary daily observations by Mr Clement Wragge in 1881—82   The buildings were vested in the Royal Society of Edinburgh, but the observatory was controlled and managed by a committee of the Meteorological Society   The observations at the summit were made by eye readings at each hour, day and night, from 1883 till the close of September, 1904, and, at the same time, observations were made at Fort William for comparison, until an observatory, with self-recording instruments, was established there by the Meteorological Council in 1890   In 1900 it was found that the funds available were insufficient for continued maintenance of the two observatories, and an appeal for additional assistance from Government funds ended in 1905, after prolonged discussion, in a misunderstanding, and to the regret of many meteorologists in all countries the observatories were closed   The results obtained fill a series of volumes of the 'Transactions of the Royal Society of Edinburgh,' and form a very notable example of meteorological enterprise and industry , the enthusiasm for the collection of data from all parts of the world which was stimulated by the successes of Buchan's first ten years at the Society had led to the collection of more material than the actual workers could deal with. The British meteorologists of the sixties of the last century—Buchan, Mitchell, Milne-Holme, and Stevenson in Scotland , with Strachey, Galton, Baxendell, in England—had grown old or passed away without any apparent successors, and in the meantime various circumstances had led to the disassociation of what Buchan had called a new science from the established sciences as recognised by universities.   There is on that account a note of sadness about the close of the careers of the British meteorologists of the nineteenth century who survived until the twentieth, among whom Buchan had achieved most.

His merits were recognised in many ways   From the Royal Society of Edinburgh he received the Makdougall–Brisbane Medal in 1876, and the Gunning Prize in 1893 ; Glasgow conferred upon him the honorary degree of LL.D. in 1887 ; he was elected F.R.S. in 1898 ; and in 1901 he was the first recipient of the medal founded by the Royal Meteorological Society of London in commemoration of G J. Symons.   He was honorary member of the Royal Society of Sciences of Upsala, the Philosophical Societies of Glasgow, Manchester, and Emden, and of the Meteorological Societies of Austria, Germany, Algiers, Mauritius, and elsewhere   He was President of the Edinburgh Botanical Society in 1870–71.

W. N. S.

SIR WALTER NOEL HARTLEY, 1846-1913

WALTER NOEL HARTLEY was born at Lichfield on February 3, 1846 His father, Thomas Hartley, was a portrait painter, some of whose works are in the collection of works by Yorkshire artists at the York Museum, and his mother's maiden name was Caroline Lockwood

He was educated privately and in 1863 he went to the Edinburgh University with the intention of studying medicine With this object he attended the usual first year's classes, including chemistry under Prof Lyon Playfair, whose laboratory he also attended   Here he made the acquaintance of the late Dr Arthur Gamgee, who advised him to devote himself entirely to chemistry This suggestion he adopted, and in later years he often expressed to me his gratitude for the interest which Gamgee took and the influence which he exercised over his early studies. It was doubtless under Gamgee's advice that he determined to go abroad to continue his studies in one of the numerous German laboratories which were already famous Consequently his stay at Edinburgh did not extend beyond one year

In the autumn of 1864, Hartley went to Germany with the intention of working in Bunsen's laboratory. Unfortunately, when he arrived at Heidelberg, he found that every place in the laboratory was already occupied In these circumstances he consulted Bunsen as to what he should do, and was recommended by him to Kolbe, his successor in the Chair of Chemistry at Marburg. Here he spent the winter of 1864-5, and it was as his fellow-student in Kolbe's laboratory in the summer session of 1865 that I made his acquaintance, which ripened into a lifelong friendship In later years we frequently looked back on the days spent in Marburg as an opportunity of knowing, by living and working in it, the conditions of student life as it had been for generations in a small German university.

The picturesque little town of Marburg had, in 1865, a population of about 7500 inhabitants and the University numbered no more than 200 students.

According to 'Minerva' of 1913, in the summer session of 1912 the students numbered 2238, including 129 women. It would be difficult to express more shortly or more clearly than by these figures, the change of conditions which has taken place in less than half a century and in the lifetime of one man.

To spend a year at the student-age working in a laboratory rendered famous by the names of Bunsen and Kolbe, and in such picturesque and old-world surroundings, appealed to Hartley's scientific and artistic tastes in a way that nothing else could. In our intercourse, Marburg memories never lost their freshness In contrast to the town, Kolbe's laboratory was almost cosmopolitan In the summer of 1865 there worked in it four British subjects, four Russians including Menschutkin, afterwards professor in Petersburg, and Saytseff, professor in Kasan, besides other nationalities, so that not more than one-half of the students were of German nationality. Kolbe did not interest

himself in his students outside of their work, but in it he was painstaking and always illuminating His somewhat stiff appearance and manner were most conspicuous in his lectures, delivered with all the crisp precision of his Hanoverian pronunciation He was called to Leipzig in the autumn of 1865, and within a year afterwards Kurhessen had ceased to exist and Marburg was no longer a *Landes-Universität.*

After returning to England Hartley filled several different posts He was for some time assistant to Dr Angus Smith in Manchester, and the experience which he gained there bore fruit in his later work on ventilation and sanitation. He was also for some time assistant to Dr Thudicum when he was occupied with the investigation of wines In connection with this work he became an enthusiastic student of Pasteur's researches, which were only then beginning to attract general attention out of France. Afterwards he was assistant to Prof Odling at the Royal Institution, and to the time which he spent there he always looked back as the happiest period of his life It was here that he did his first great experimental research For it he had been well prepared by his work on wine in Thudicum's laboratory and his reading in connection with it At the Royal Institution, in constant association with so inspiring a personality as Dr Odling, and under the same roof with Tyndall elaborating his work and delivering his lectures on Dust and Disease, he found himself in the environment most favourable for the production of a masterpiece like his "Experiments concerning the Evolution of Life from Lifeless Matter" which was communicated to the Royal Society by Dr Odling and was published in its 'Proceedings,' vol 20, pp 140–157 (1872).

This investigation was undertaken in order to test the validity of the conclusion arrived at by Dr Charlton Bastian in a paper published in 'Nature' of June 30, 1870, entitled "Facts and Reasonings concerning the Heterogeneous Evolution of Living Things"

According to Hartley the most remarkable case described in this paper was that of Experiment 19, in which Bastian gave a drawing of a large organised mass obtained from a solution of sodium phosphate and ammonium tartrate, which had been exposed to a temperature varying between $146°$ C and $153°$ C, for four hours This organism was seen to grow within the flask till it attained a certain size, beyond which it did not increase Hartley proceeds :— "Now a fact so distinctly stated as the production of an organism, and its development to a considerable size, from a liquid containing nothing further than phosphate of soda and tartrate of ammonia, in a flask from which the air had been most thoroughly withdrawn, and which when containing the liquid and hermetically sealed, had been heated to so high a temperature, was (admitting the conditions and performance of the experiments to be faultless) an absolute proof of the evolution of living matter *de novo*. For my own satisfaction I determined to commence a series of careful experiments in some cases adhering strictly to the conditions of those made by Dr. Bastian ; but it was necessary to devise some refinement on the mode of examining the liquids experimented on without exposure to atmospheric air."

In this research Hartley showed perhaps for the first time his extraordinary resources as an experimenter, which became afterwards so well known. In those days the experimenter had to make all his own apparatus, and this paper is worthy of being read for the clever way in which the innumerable difficulties to be met with in such an investigation were overcome. It will be sufficient here to refer to his use of hydrogen gas as a sterile atmosphere, in which he transferred the liquids from the heated tubes to the slides for microscopic examination.

The tubes containing sodium phosphate and ammonium tartrate were heated for a number of hours to temperatures lying between 110° C and 150° C. They were then kept unopened at temperatures ranging from 24° to 34° C., for different intervals of time ranging from two months to a year, without any form of life being visible in their contents. After opening the tubes and transferring some of their contents, in the sterilised atmosphere to the plates, nothing living was discovered. When the liquids after prolonged preservation in sealed tubes were exposed to air filtered through cotton wool and kept at a temperature of 30° to 34° C during the day-time and not below 24° C at night, they remained quite unaltered, although kept for over a month. When, however, the liquids which, after prolonged keeping without development of life, were afterwards exposed to ordinary air at a temperature ranging between 24° and 34° C, they rapidly became turbid and full of living organisms.

Although Hartley thus showed that when he repeated Bastian's experiments, taking those precautions which his experience and study taught him were necessary to exclude all contamination by the atmosphere, no living organisms appeared, and that when these lifeless liquids were allowed to come in contact with unfiltered air, living organisms quickly appeared and multiplied, this did not prove that the organisms which appeared in Bastian's tubes were not spontaneously evolved in them, because, in logic, it is impossible to prove a universal negative, but it did raise the question—is it less likely that Bastian was not quite successful in completely protecting his solutions from contact with the air, admittedly a difficult experimental operation, than that living organisms were generated in a sterile liquid by some power or process which is not specified?

Considered simply as a question of probability the chance of the accidental contamination of the contents of the tubes by air is so much greater than that of the production of life out of lifeless matter, which had never before been observed, that it must be accepted as equivalent almost to a certainty. The publication of this paper was delayed for nearly a year by a very serious illness, to which Hartley nearly succumbed.

In the year 1871 Hartley became Senior Demonstrator in the laboratory of King's College, London, under Prof. Bloxam, where he remained until 1879, when he was made Professor of Chemistry in the Royal College of Science, Dublin. In 1882 he married Mary Laffan, the well-known writer of Irish fiction, and daughter of the late Michael Laffan, of Blackrook, co Dublin. Among her most successful books may be cited 'Hogan, M.P.,'

and 'Flitters, Tatters, and the Councillor' He remained in Dublin until he was retired under the age limit, when he received the honour of Knighthood While at King's College he did much important original work, including his remarkable researches on the fluid cavities in minerals, in which he was the first to utilise Andrews' discovery of the critical point of gases for the determination of the nature of the liquids found in even microscopic cavities The experimental method which he devised for this purpose was, as all his methods were, simple, ingenious, and effective

It was when he had finished this work, and while still at King's College, that he began in earnest the spectrographic studies which he pursued to the very end and by which he is principally known *

The value attached abroad to his work in this field is well shown by the invitation extended to him by Prof. Kayser, of Bonn, to write the part relating to absorption spectra in his well-known 'Handbuch der Spectroscopie,' 1905 In the preface to the third volume he writes "Das dritte Kapitel danke ich Prof W N. Hartley in Dublin der mehr als alle übrigen Forscher zusammen über die Frage des Zusammenhanges zwischen Constitution und absorption gearbeitet hat, und der mir daher in erster Linie berufen schien eine zusammenfassende Darstellung zu geben, etc." If Hartley's work had been confined to absorption spectra this would be sufficient testimony to its value for the present purpose· but this was only one part of his spectroscopic work, and, though important, perhaps not the most important part of it I am indebted to Dr W. E. Adeney, who was so intimately associated with Hartley, for a summary of his spectrographic work in general. It is taken from the report submitted by Dr Adeney to the Senate of the Royal University of Ireland in support of a motion to confer on him the degree of D Sc. *honoris causa.*

" Prof. Hartley discovered a method by which, with unachromatised lenses, he was able to photograph entire spectra on a single plate including red rays and these far in the ultra-violet. He was the first to apply dry plate photography to the purposes of studying spectra in 1877 During the succeeding twenty years he carried out a series of researches establishing the relationship between the molecular structure of carbon compounds and their absorption spectra. He has applied the knowledge thus acquired to determining the molecular constitution of complex organic substances, the identification of poisonous alkaloids, an important matter in medico-legal analysis, and to the solution of various difficult and abstruse problems in the subject of organic chemistry.

" He demonstrated the physical relationship of such derivatives of coal tar as benzene and naphthalene to the brilliant dyes which are derived from

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* It is more than probable that the finding of several pieces of the apparatus used at an earlier date in similar work by Dr William Allen Millar finally directed Hartley's mind towards this line of research Some of this earlier photographic apparatus he actually employed in his first experiments at King's College, and it was when there that he got his first grant from the Royal Society for the purpose of the investigation.

them, and explained that the former substances, which to the human eye are colourless, are in reality coloured, but the vibrations are so rapid that the eye cannot perceive them, though by retarding the vibrations visible colour is developed Hence we have colours visible and invisible. He has explained the cause of the absorption spectra of organic bodies to be due to their molecular and intramolecular vibrations and has calculated from the velocity of light the mean rates of vibration of the molecules of benzene, naphthalene, and anthracene He has studied the absorption spectra of the different constituents of the atmosphere, and shown that the abrupt limitations of the sun's spectrum, which is short as compared with that of electric light, can be caused by no other constituent of the atmosphere than ozone, which exerts an extraordinary absorptional power on the ultra-violet rays

"He was the first to show in 1883 the inter-relationship of the spectra of the elements, when classified according to the periodic law, and by the discovery that the spectra of magnesium, zinc, and cadmium are the result of three series of harmonic vibrations with similar intervals, the fundamental vibrations of which differ only in pitch, he was the first to recognise the law of homologues in the spectra of the elements. This law was recognised independently in 1885 by Prof J R Rydberg, of Stockholm, and has since been elaborately studied by him and by Profs. Kayser and Runge.

"Prof. Hartley's facts pointed to the conclusion that metallic elements, having certain chemical properties in common and whose atomic weights differ by approximately constant quantities, and whose spectra are similarly constituted, are molecules of the same kind of matter but in different states of condensation

"He applied his observations to deciding the question as to the true position of the metal beryllium in the classification of the elements. In association with some of his students he carried out a series of original investigations on the spectra of some thirty of the elements and amongst the wave-lengths of the spark spectra, which he published in conjunction with Dr W. E. Adeney, are those of the lines due to air, which are of such importance in all spark spectra observations. He devised simple and extremely delicate methods of analysis which have led to the discovery of the wide distribution of several rare substances and of their mode of occurrence in minute proportions in a large number of common ores and minerals, in meteorites and metallurgical materials and products. He was the first to discover the presence of the rare earth yttria in any British mineral

"By exact investigations on the spectra of the flame seen in the manufacture of steel by the Bessemer process he has shown that the metals iron and manganese are largely vaporised in the operation, which is evidence of the very high temperature attained He took several series of photographs of spectra during intervals of half a minute during the entire course of the process, and explained, from a study of them, the thermochemistry of the changes brought about in the refining of iron.

"He has applied the study of the spectra of starch, sugars, and the albuminoids from grain, to the decision of questions connected with the industries of brewing and distilling

"The work executed by Prof Hartley and Mr Ramage with the great spectrometer of the Royal University, namely, the proof of the existence of gallium in the sun, has recently been confirmed in the United States by Prof. Rowland, of Baltimore "*

I am much indebted to Messrs. Adeney and Dobbie for supplying these notes, it would have been outside my competence to do so

The bulk of Hartley's spectroscopic work was done after he went to Dublin in 1879, and from that time onwards I saw him only in the holidays From 1878 to 1881 I was fortunate in usually getting him to spend part of the summer with me while carrying out sounding and dredging operations in the steam yacht "Mallard," which I had built after the return of the "Challenger" for the study of the Scottish seas

During the voyage of the "Challenger" Hartley was my only regular correspondent outside of my family, and he hardly ever missed a mail. In August, 1913, while at Braemar for his health, I had to make the voyage to the Cape for my own health, and I asked him to let me have a letter from him when at the Cape as a remembrance of old times. I got the letter, cheerful and hopeful; but, before I received it, he was no more.

During the long summer days on the West Coast of Scotland he interested

* In supplement of the above report by Dr Adeney the following notes regarding later work have been kindly supplied by Dr James J Dobbie, F R.S —

"In 1898 Hartley commenced a study of the relation between the spectra and constitution of tautomeric substances in conjunction with James J Dobbie Isatin and carbostyril were first selected for investigation Each of these bodies gives rise to two stable methyl-derivatives, one of which had been proved by satisfactory chemical evidence to possess the 'lactam,' the other the 'lactime' constitution The constitution of isatin and carbostyril themselves, however, had not been determined with certainty, the chemical evidence pointing partly in one direction, partly in the other By comparing the absorption spectra of the parent substances with those of their methyl-derivatives it was at once obvious that they were practically identical with the spectra of the derivatives to which the lactam constitution had been assigned, viz. methyl-pseudo-isatin and methyl-pseudo-carbostyril Convincing evidence was thus afforded that isatin and carbostyril are themselves lactams and not lactimes. This method of investigation was afterwards applied to a large number of substances, including the ethyl esters of dibenzoylsuccinic acid, o-oxycarbanil, and phloroglucinol, and has proved a valuable aid to the chemist in the study of the obscure phenomena of tautomerism. It possesses the great advantage over the usual chemical methods of attacking constitutional problems, that the possibility of molecular rearrangement occurring during the examination is practically excluded

"In the course of these investigations the optical isomerides benzanti- and benzsyn-aldoxime were examined and found to possess the same absorption spectra. This observation has proved to be of considerable practical value especially in the investigation of alkaloids, as it provides a ready means of deciding whether two alkaloids having the same composition and molecular weight are structural or optical isomerides."

himself much in my work, and was, entertaining as well as instructive when talking of his own work. His many-sidedness made him a particularly interesting companion

It was during one of these cruises that he told me about his experiments with chlorophyll and its absorption spectrum   During the expedition of the " Dacia " in 1883, I obtained from one of the " oceanic shoals," the discovery of which marked a change of view and of practice in deep-sea sounding, fragments of shell and calcareous rock, coloured green, and, when preserved in spirit, the green colouring matter transferred itself to the spirit and coloured it green   On my return home I sent the spirit to Hartley, thinking it would interest him. He examined it spectroscopically and found that the colouring matter was chlorophyll   He then experimented on some spirit rendered purple by the colouring matter of Holothurians from great depths and found that this also was a variety of chlorophyll.

This was a most important discovery of Hartley's, for which he has not received sufficient credit.   It at once explained the colour of the band of green water found on the western oceanic shores of continents in tropical regions, where the water is abnormally cold and generally of an intensely green colour.   The low temperature and the green colour are characteristic of the abysmal water, which in these regions rises to the surface, in order to make good the drain of warm surface water, removed by the Trade winds blowing off shore

Of equal importance with his work on absorption-spectra was that on the spectra of the elements in the oxy-hydrogen blowpipe and its application to the study of the Bessemer flame.   The importance of the latter was very far-reaching.   In all his experimental work the primary interest for Hartley was the trustworthiness of his methods and the exactness of his results. But there were interests for him beyond these   All that he did was illuminated by his inherited artistic feeling and by his conception of the place which the results of his work would take in general Natural History. Hartley was a follower of Lord Kelvin, who always used to call himself a Naturalist.   He held that Inorganic Natural History is as extensive and as important as Organic Natural History.   The importance of his Bessemer work for Natural History was fixed in my memory by the picturesque account which he gave of a day's excursion from Malvern, where he was staying for the benefit of his health

The weather being fine and clear, he walked up to the high ground in the neighbourhood, whence there was an uninterrupted view in the direction of the great centres of the Midland steel industry.   There he sat down and waited until, from his familiarity with the routine in such works, he knew that the " Bessemer blow " would be started   Then one metallic eruption after another appeared on the horizon, each forming its own " pillar of cloud," which gradually drifted over the plain, getting thinner as it spread out, and shedding by degrees its metallic contents over the surface of the ground.   His graphic description of this scene made a great impression on

me, and it furnished a fresh illustration of how manifold are the ways in which strange matter can be distributed over the surface of the earth

Incidents such as these show how informing Hartley was in ordinary intercourse, especially when artistic influences made themselves felt He was very reserved, and this was perhaps due to a slight deafness, which troubled him all his life Though reserved, he was full of human sympathy, and never forgot any act of kindness in others

Although hampered all his life by frail health and by none too easy circumstances, he turned out an amount of first-rate work that the most robust might be proud of He was a rapid worker Helped largely by his keen insight and full knowledge, he obtained results from which he deduced accurate conclusions without loss of time over minute details It will be some time before all his work has been completely assimilated by Science. In 1906 he received the Longstaff medal from the Chemical Society, in recognition of the great value of his scientific work

With his retirement from the active duties of his professorship his experimental work ceased, and at the same time his health became more and more uncertain For this he tried various changes of scene, but without much success. Finally, in the summer of 1913, he went to the Aberdeenshire Highlands, a district which he knew well and with which he had old associations While there the fine mountain climate relieved his suffering and raised his spirits, and, being naturally very sanguine, he was looking forward to a more lasting relief of his troubles than he had experienced. This feeling seemed to give him too much confidence, and, in his enjoyment of the exhilarating air and scenery he overstrained his bodily powers, but not so as to cause any anxiety It was fatigue which would be dissipated by a night's rest He went to bed and passed away peacefully in his sleep

He is survived by Lady Hartley and by their only son, W J Hartley, teacher in Agricultural Bacteriology in the University College, Cardiff.

It is, perhaps, more than a coincidence that the son should devote himself for life to the subject in which his father first made a name in Science But at that date the subject was new and the word " Bacteriology " had not been coined. If circumstances had been different, I have Hartley's own word for it that his career would certainly have been different When talking recently about his early work in the laboratory of the Royal Institution he said to me "If I could have afforded it I should have stuck to Bacteriology." Unfortunately, in 1872 there was not the possibility of earning a livelihood in it. What Bacteriology lost Chemistry and Physics gained

J. Y. B

HUGH MARSHALL, 1868-1913.

HUGH MARSHALL was born in Edinburgh, January 7, 1868, and was educated at the Moray House Normal School   On leaving school he applied himself to the study of Chemistry, at first under Dr Drinkwater, and afterwards in the Chemistry Department of the University of Edinburgh. He also attended the classes in the curriculum for Degrees in Science, and in 1886 graduated as B Sc.   In 1887 the Gunning "Joseph Black" Prize and the Mackay Smith Scholarship in Chemistry were awarded to him.   In the same year he was appointed one of the assistants in the Chemistry Department.   On two occasions he obtained leave of absence for a summer session and spent the time at Munich with Profs. Groth and Krüss, and in Ghent with Prof Renard, in the further study of Mineralogy and Crystallography   In 1890 he graduated as D Sc , the subject of his thesis being the work on the eléctrolytic oxidation of cobaltous salts described below   In 1894 he was appointed Lecturer on Mineralogy and Crystallography, and in 1902 Lecturer on Chemistry.   On the appointment of Prof Walker, in 1908, to the Chair of Chemistry in Edinburgh, Dr Marshall succeeded him in Dundee

Dr Marshall became a Fellow of the Royal Society of Edinburgh in 1888, of the Chemical Society in 1889, and of this Society in 1904   He was also a corresponding Member of the Mexican Scientific Society "Antonio Alzate." In 1904 the Council of the Royal Society of Edinburgh awarded to him the Keith Prize for the discovery of the persulphates. He also held the Keith Medal of the Royal Scottish Society of Arts, and a Medal of the Edinburgh Association of Science and Arts for his invention of the "Petrolite" lamp, an ingenious arrangement for the safe burning of volatile hydrocarbons.   .

At the close of the summer session of 1913, he went, as captain of the Dundee company of the St. Andrews University Officers' Training Corps, to camp at Ilkley. After the training he went to Paris, but not feeling well returned to London. There it was discovered that he was suffering from enteric fever. He died in London on September 5.

Prof Marshall was a very able and successful teacher, and gave a great deal of time and thought to this part of his work, but yet was able to make important contributions to our knowledge of Chemistry.

He took a great interest in the application of electrolysis to the separation and quantitative determination of metals, and, in repeating Classen's separation of copper and cobalt, observed that after all the copper must have been deposited, the solution was green, and that further electrolysis did not change the colour. To this green liquid he added sulphuretted hydrogen, which produced a white cloudiness due to separated sulphur, while the liquid became pink . it was obvious that there was no copper in the solution and

that some of the cobaltous salt had been oxidised   This observation led him to examine the electrolytic oxidation of cobaltous salts   By using a divided cell, with dilute sulphuric acid in the cathode compartment, and solution of cobaltous sulphate and sulphuric acid in the anode compartment, he obtained pure crystallised cobaltic sulphate, and from this prepared potassium and ammonium cobaltic alums, in blue octahedra, with 24 molecules of water, exactly as in the well known alums

While engaged in this investigation, he observed that in the electrolysis of a solution containing potassium hydrogen sulphate along with cobaltous sulphate and sulphuric acid, there were deposited in the anode compartment not only crystals of potassium cobaltic alum, but also small colourless crystals   These he collected and examined, and found that they consisted of potassium persulphate   He followed up this incidental discovery, and prepared directly by electrolysis potassium and ammonium persulphates, and from them, by double decomposition, other persulphates

Berthelot had, in 1878, obtained persulphuric anhydride, S_2O_7, by the action of the silent electric discharge on a mixture of sulphurous anhydride and oxygen   When dissolved in water this gave an acid solution which quickly decomposed giving off oxygen and leaving sulphuric acid   Berthelot obtained a similar solution by the electrolysis of sulphuric acid   By cautiously neutralising this unstable solution with baryta, he obtained, besides a precipitate of barium sulphate, a solution gradually decomposing into oxygen, barium sulphate and sulphuric acid   This soluble barium salt could be nothing but barium persulphate, but Berthelot was unable to isolate it, and fourteen years later, in welcoming Marshall's discovery, speaks of the persulphates as hitherto only dimly seen

Dr Marshall studied the oxidising action of the persulphates, showing its analogy to that of the halogens, in giving, for instance, tetrathionates from thiosulphates   He showed the remarkable modification of the oxidising action caused by the presence of even a small quantity of a soluble silver salt.   Persulphates precipitate peroxide of manganese from a solution of a manganous salt, but in the presence of a soluble silver salt the manganese is oxidised to permanganic acid.   Marshall referred this action to silver peroxide continuously formed and reduced, the action of the silver peroxide on the manganous salt being similar to that of lead peroxide in Walter Crum's test for manganese.   He further showed how persulphate with silver nitrate can be used for the colorimetric determination of even very minute quantities of manganese.

Dr. Marshall at first, misled by an error in the published results of conductivity measurements in the case of potassium perchlorate, preferred the simple formula KSO_4, but when the error was pointed out and corrected, he at once adopted the double formula $K_2S_2O_8$, which as Bredig and also Moeller showed agrees with other physical properties.

The work on the oxidation of cobaltous salts was published in the Chemical Society's 'Transactions,' September, 1891.   A note on the persulphates was

read before the Royal Society of Edinburgh on February 16, 1891, and printed in the 'Proceedings' A much fuller account of this work is contained in the Chemical Society's 'Transactions,' September, 1891 In 1897 Dr. Marshall published in the 'Journal of the Society of Chemical Industry' a paper on the manufacture and industrial uses of the persulphates.

He wrote the report on Inorganic Chemistry for the Chemical Society in 1896 and 1897. He translated into English Prof. Groth's 'Introduction to Chemical Crystallography'

By Prof Marshall's death Science has lost an acute and original investigator and a zealous and sound teacher: all who knew him personally mourn a very true and hearty friend

A. C. B.

ALEXANDER ROSS CLARKE, 1828—1914

ALEXANDER ROSS CLARKE was born on December 16, 1828, he came of an old Highland family in Sutherlandshire. After an ordinary school education he, somewhat suddenly, formed the desire to join the Army and presented himself for the entrance examination for the Royal Military Academy, Woolwich. The time allowed him for preparation, only about three weeks, naturally did not permit him to take his just place, he was successful but his name was somewhat low on the list Once at Woolwich, however, he rapidly worked his way up and in the passing out examination gained the first place and obtained his commission as a second lieutenant in the Royal Engineers in 1847. He was posted to the Ordnance Survey at Southampton in 1850, he was quartered in Canada from 1851 to 1854, in which latter year he returned to the Ordnance Survey and spent in it the whole remainder of his service until his retirement as lieutenant-colonel in 1881.

In 1856 he took charge of the Trigonometrical and Levelling departments. The work of the Principal Triangulation had been completed in the field in 1851 and Clarke's first task was to reduce the observations and discuss and publish the results. This he accomplished with extraordinary rapidity; the great volume on the "Account of the Observations and Calculations of the Principal Triangulation and of the Figure, Dimensions and Mean Specific Gravity of the Earth as derived therefrom" was published in 1858.

To appreciate the magnitude of this achievement it must be remembered that the methods of geodetical calculation were then by no means in the comparatively simple form they have since assumed. The first half of the nineteenth century had seen a great development in the practice both of

observation and of reduction of geodesy.   The work of Gauss, Bessel and later
of Struve had perfected the system of calculation, at the same time rendering
it more laborious, by the introduction of least square adjustments.   Struve's
work was, however, not published, except in part, and the account of the
Great Triangulation of India was in such a cumbrous form and the calcula-
tions were so voluminous, clerical labour being then very cheap in India, that
the precedent of Indian work was of little value when applied to British
conditions   Clarke followed Bessel (*Gradmessung in Ostpreussen*) closely and
the whole network of triangles covering the British Isles was broken up into
a series of 21 figures, the most complicated figure involving the solution of
64 equations of condition and the average figure of 44.

This is not the place to undertake any discussion of the technical details,
but as directly bearing upon Clarke's work it may be briefly stated that the
results of modern re-observation most amply justify his procedure and seem to
show that his method of reduction got out of the observed quantities a final
result as accurate as could possibly be obtained.   Though modern practice
has in certain particulars greatly simplified such work, and though the
rigorous reduction of such a complex network will probably never again be
undertaken, Clarke's volume must always remain a model.

In 1860 the Russian Government invited the co-operation of the Govern-
ments of England, France, Germany and Belgium in the measurement of a
longitudinal arc from Valentia, in Ireland, to Orsk.   An essential preliminary
was the comparison of the various national standards of length, a task which
was entrusted to Clarke and was carried out by him in a specially designed
room built at the Ordnance Survey Office   The results of this, which included
also the standardisation of 10-foot bars for India and Australia, was published
in 1866 and Clarke took the opportunity of rediscussing the figure of the
earth.   In this he exhibited the same genius for calculation already evident
in his previous work   In 1878 he again returned to this subject and incor-
porated further elements in the form of longitudinal arcs observed in India,
as well as improved values for Indian, Anglo-French, and Russian meridional
arcs.   The result showed that the Indian and European elements were not
very consistent, that is to say they could not be combined into a spheroid of
revolution, and though they could be better harmonised by an ellipsoid of
three unequal axes it was not quite clear how far this concordance was due
to actual ellipticity of the equator and how far to the apparent diminution of
the residuals which would necessarily follow the substitution of three unequal
axes for two axes in the computations

However this may be, and modern geodesists would say that the earth, that
is to say the geoid or surface to which the plumb line is everywhere normal,
is neither a spheroid nor an ellipsoid, for all practical purposes Clarke's
results stand good.

In 1861 he published the abstracts of spirit levelling in England, Wales,
and Scotland.   In this same year it was decided to re-observe the connection
between the English and Continental triangulations, a necessary link in the

longitudinal arc already mentioned. The junction of England and France, in order to determine the difference of position between Greenwich and Paris Observatories, had been originally made in 1783–87 and repeated in 1821–23 Now that the principal triangulation of England was completed it appeared probable that the connection might be considerably improved, and to that end the British, French, and Belgian Governments co-operated and three English stations were connected with two French and four Belgian. Clarke was mainly responsible for the arrangement of the work and himself observed at the English stations   In 1863 he published the account and reductions.

In 1880 he embodied his accumulated experience in his "Geodesy" which remains still, on the whole, the best book on the subject in any language

In 1881 he retired from the Ordnance Survey and from the Army   His retirement was nothing short of a disaster to the national survey, there being no other member of the staff who had Clarke's scientific attainments or mathematical knowledge.

Clarke is credited with seventeen entries in the Royal Society's 'Catalogue of Scientific Papers,' all on his own subject with the exception of one slight incursion into the theory of music   He was elected a Fellow in 1862 and received the Royal Medal in 1887 for his comparison of the standards of length and his determination of the figure of the earth   He was created a Companion of the Bath in 1870.

In 1883 he and the Astronomer Royal were appointed delegates to the International Geodetic Congress.   From that time up to his death on February 11, 1914, he lived a retired life, taking no share in any public scientific activities

He married in 1853 Frances, daughter of the late Major-General Dixon, R.E , she died in 1888, leaving eight children, five daughters and three sons, who survive their father.

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INDEX to VOL. XC. (A)

END OF THE NINETIETH VOLUME (SERIES A)

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VOL. XC.—A. *d*